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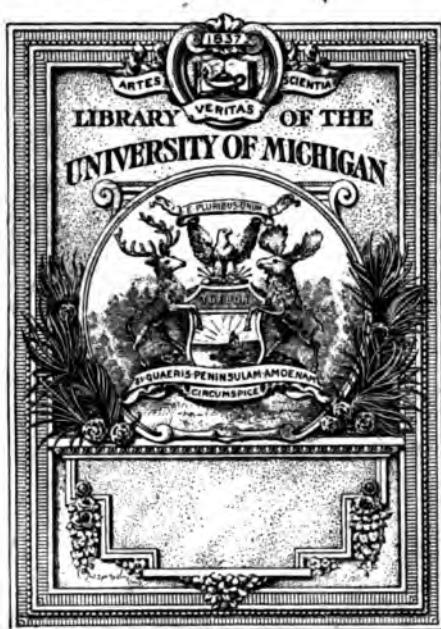
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SERIES A
CONTAINING PAPERS OF A MATHEMATICAL AND
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CONTENTS.



SERIES A. VOL. LXXX.

No. A 535.—December 9, 1907.

| | PAGE |
|--|------|
| The Annealing of Copper : with Special Reference to Dilatation. By T. Turner, M.Sc., A.R.S.M., Professor of Metallurgy, and D. M. Levy, A.R.S.M., Assistant Lecturer in Metallurgy, University of Birmingham. Communicated by Professor J. H. Poynting, F.R.S..... | 1 |
| A New Current Weigher, and a Determination of the Electromotive Force of the Normal Weston Cadmium Cell. By Professor W. E. Ayrton, F.R.S., and T. Mather, F.R.S., Central Technical College, London, and F. E. Smith, A.R.C.S., National Physical Laboratory, Teddington. (Abstract)..... | 12 |
| On Luminous Efficiency and the Mechanical Equivalent of Light. By Charles V. Drysdale, D.Sc. Communicated by Silvanus P. Thompson, D.Sc., F.R.S. (Abstract)..... | 19 |
| On the Surface-tension of Liquids investigated by the Method of Jet Vibration. By P. O. Pedersen, Copenhagen. Communicated by Lord Rayleigh, P.R.S. (Abstract) | 26 |
| The Dispersion of Double Refraction in Relation to Crystal Structure. By T. H. Havelock, M.A., D.Sc., Fellow of St. John's College, Cambridge, Lecturer in Applied Mathematics in Armstrong College, Newcastle-on-Tyne. Communicated by Professor J. Larmor, Sec. R.S. | 28 |
| Experiments on a New Cathode Dark Space in Helium and Hydrogen. By F. W. Aston, A.I.C., Research Scholar, the University of Birmingham. Communicated by Professor J. H. Poynting, F.R.S. (Plate 1) | 45 |
| On the Presence of Sulphur in some of the Hotter Stars. By Sir Norman Lockyer, K.C.B., LL.D., Sc.D., F.R.S. (Plate 2)..... | 50 |
| Note on the Association of Helium and Thorium in Minerals. By the Hon. R. J. Strutt, F.R.S. | 56 |
| On the Measurement of Temperatures in the Cylinder of a Gas Engine. By Professor H. L. Callendar, F.R.S., and Professor W. E. Dalby, M.A., M.Inst.C.E. | 57 |
| On the Normal Weston Cadmium Cell. By F. E. Smith, A.R.C.Sc. Communicated by R. T. Glazebrook, F.R.S. (Abstract) | 75 |
| The Silver Voltameter. Part I.—By F. E. Smith, A.R.C.Sc., and T. Mather, F.R.S. Part II.—By F. E. Smith, A.R.C.Sc., and T. M. Lowry, D.Sc. Communicated by R. T. Glazebrook, F.R.S. (Abstract) | 77 |
| The Diurnal Variation of Terrestrial Magnetism. By Arthur Schuster, F.R.S. (Abstract)..... | 80 |

No. A 536.—February 13, 1908.

| | PAGE |
|--|------|
| Results of the Interaction of Mercury with Alloys of other Metals. By J. W. Mallet, F.R.S., University of Virginia | 83 |
| A Method of Depositing Copper upon Glass from Aqueous Solutions in a Thin Brilliantly Reflecting Film, and thus producing a Copper Mirror. By F. D. Chattaway, F.R.S. | 88 |
| The Electric Discharge in Monatomic Gases. By Frederick Soddy, M.A., Lecturer in Physical Chemistry in the University of Glasgow, and Thomas D. Mackenzie, B.Sc., Carnegie Research Scholar. Communicated by Professor J. Larmor, Sec. R.S. | 92 |
| Note on the Sensibility of the Ear to the Direction of Explosive Sounds. By A. Mallock, F.R.S. | 110 |
| Magnetic Declination at Kew Observatory, 1890—1900. By C. Chree, Sc.D., LL.D., F.R.S., Superintendent, Observatory Department, National Physical Laboratory. (Abstract) | 113 |
| On the Frictional Resistances to the Flow of Air through a Pipe. By John H. Grindley, D.Sc. (Vict.), and A. H. Gibson, M.Sc. (Vict.) Communicated by Professor Horace Lamb, F.R.S. | 114 |
| Exterior Ballistics. (No. 2.) By George Forbes, F.R.S. | 140 |
| The Effects of Temperature and Pressure on the Thermal Conductivities of Solids. Part II.—The Effect of Low Temperatures on the Thermal Conductivities of Pure Metals and Alloys. By Charles H. Lees, D.Sc., F.R.S., Professor of Physics in the East London College, University of London. (Abstract) | 143 |
| The Action of Ozone on Water-colour Pigments. By Sir William de W. Abney, K.C.B., F.R.S..... | 146 |
| Preliminary Note on the Operational Invariants of a Binary Quantic. By Major P. A. MacMahon, D.Sc., F.R.S. | 151 |

No. A 537.—March 5, 1908.

| | |
|---|-----|
| The Absorption Spectra of the Vapours of Benzene and its Homologues at Different Temperatures and Pressures, and likewise of Solutions of Benzene. By Walter Noel Hartley, F.R.S., D.Sc., Royal College of Science, Dublin. (Abstract)..... | 162 |
| Further Consideration of the Stability of the Pear-shaped Figure of a Rotating Mass of Liquid. By Sir G. H. Darwin, K.C.B., F.R.S., Plumian Professor of Astronomy, and Fellow of Trinity College, Cambridge. (Abstract) | 166 |
| On Kinetic Stability. By Horace Lamb, F.R.S..... | 168 |
| Prominence and Coronal Structure. By William J. S. Lockyer, M.A., Ph.D., F.R.A.S., Chief Assistant, Solar Physics Observatory, South Kensington. Communicated by Sir Norman Lockyer, K.C.B., LL.D., Sc.D., F.R.S., Director of the Solar Physics Observatory. (Plate 3) | 178 |
| The Conversion of Diamond into Coke in High Vacuum by Cathode Rays. By the Hon. Charles A. Parsons, C.B., F.R.S., and Alan A. Campbell Swinton..... | 184 |

| | PAGE |
|---|------|
| On the Scattering of the β -rays from Uranium by Matter. By J. A. Crowther, B.A., St. John's College, Cambridge. Communicated by Professor J. J. Thomson, F.R.S. | 186 |
| The Charges on Positive and Negative Ions in Gases. By John S. Townsend, F.R.S., Wykeham Professor of Physics, Oxford | 207 |
| On the Generation of a Luminous Glow in an Exhausted Receiver moving near an Electrostatic Field, and the Action of a Magnetic Field on the Glow so produced. By Frederick John Jervis-Smith, M.A. Oxon, F.R.S., University Lecturer in Practical Mechanics and Experimental Physics, Oxford..... | 212 |
| The Spectrum of Magnesium and of the So-called Magnesium Hydride, as obtained by Spark Discharges under Reduced Pressure. By E. E. Brooks, B.Sc., A.M.I.E.E. Communicated by Sir William Crookes, F.R.S. | 218 |
| Notes on the Application of Low Temperatures to some Chemical Problems : (1) Use of Charcoal in Vapour Density Determination ; (2) Rotatory Power of Organic Substances. By Sir James Dewar, M.A., Sc.D., LL.D., F.R.S., Jacksonian Professor in the University of Cambridge, and Humphrey Owen Jones, M.A., D.Sc., Fellow of Clare College and Jacksonian Demonstrator in the University of Cambridge | 229 |

No. A 538.—April 6, 1908.

| | |
|---|-----|
| Address of the President, Lord Rayleigh, O.M., D.C.L., at the Anniversary Meeting on November 30, 1907 | 239 |
| On the Non-Periodic or Residual Motion of Water Moving in Stationary Waves. By Mrs. Hertha Ayrton. Communicated by Professor J. H. Poynting, F.R.S. (Plates 4—6) | 252 |
| On the Perception of the Direction of Sound. By Professor C. S. Myers, M.A., M.D., and Professor H. A. Wilson, D.Sc., F.R.S., King's College, London | 260 |
| On the Intimate Structure of Crystals. Part VI.—Titanic Oxide, its Polymorphs and Isomorphs. By W. J. Sollas, Sc.D., F.R.S., Professor of Geology in the University of Oxford..... | 267 |
| Report on the Eruptions of the Soufrière in St. Vincent in 1902, and on a Visit to Montagne Pelée in Martinique. Part II.—The Changes in the Districts and the Subsequent History of the Volcanoes. By Dr. Tempest Anderson. Com- municated by Professor T. G. Bonney, F.R.S. (Abstract) | 281 |
| On the Observation of Sun and Stars made in some British Stone Circles. Third Note.—The Aberdeenshire Circles. By Sir Norman Lockyer, K.C.B., F.R.S., Hon. LL.D., Hon. Sc.D., Director Solar Physics Observatory | 285 |
| On the Determination of Viscosity at High Temperatures. By Charles E. Fawsitt, D.Sc., Ph.D., Lecturer on Metallurgical Chemistry in the University of Glasgow. Communicated by Professor Andrew Gray, F.R.S. | 290 |

No. A 539.—May 5, 1908.

| | PAGE |
|--|------|
| BAKERIAN LECTURE FOR 1907.—On the Atomic Weight of Radium. By T. E. Thorpe, C.B., LL.D., F.R.S. | 298 |
| Alternate Current Measurement. By W. E. Sumpner, D.Sc., M.I.E.E. Communicated by Professor J. Perry, F.R.S. | 310 |
| The Decomposition of Ozone by Heat. By Edgar Philip Perman, Assistant Professor of Chemistry, University College, Cardiff, and Richard Henry Greaves. Communicated by E. H. Griffiths, F.R.S. | 353 |
| Effects of Self-induction in an Iron Cylinder when traversed by Alternating Currents. By Ernest Wilson, Professor of Electrical Engineering at King's College, London. Communicated by Sir William Preece, F.R.S. | 369 |

No. A. 540.—May 25, 1908.

| | |
|--|-----|
| The Effect of Hydrogen on the Discharge of Negative Electricity from Hot Platinum. By Professor H. A. Wilson, F.R.S., King's College, London. (Abstract)..... | 379 |
| Comparison of the Board of Trade Ampere-Standard Balance with the Ayrton-Jones Current-Weigher; with an Appendix on the Electromotive Forces of Standard Cells. By T. Mather, F.R.S., Central Technical College, London, and F. E. Smith, A.R.C.S., National Physical Laboratory, Teddington | 383 |
| The Refractive Index and Dispersion of Light in Argon and Helium. By W. Burton, B.A., B.Sc., Research Student, formerly Scholar, of Emmanuel College, Cambridge. Communicated by Professor J. J. Thomson, F.R.S. | 390 |
| On the Refractive Indices of Gaseous Nitric Oxide, Sulphur Dioxide, and Sulphur Trioxide. By C. Cuthbertson, Fellow of University College, London, and E. Parr Metcalfe, B.Sc., 1851 Exhibition Scholar. Communicated by Professor F. T. Trouton, F.R.S..... | 406 |
| On the Dispersion of Gaseous Mercury, Sulphur, Phosphorus, and Helium. By C. Cuthbertson, Fellow of University College, London, and E. Parr Metcalfe, B.Sc., 1851 Exhibition Scholar. Communicated by Professor F. T. Trouton, F.R.S. | 411 |
| On the Electrical Resistance of Moving Matter. By Professor F. T. Trouton, F.R.S., and A. O. Rankine, B.Sc., University College, London | 420 |
| The Relation between Wind Velocity at 1000 Metres Altitude and the Surface Pressure Distribution. By E. Gold, M.A., Fellow of St. John's College, Cambridge. Communicated by Dr. W. N. Shaw, F.R.S. | 436 |
| On the Polymorphic Changes of Ammonium Nitrate. By U. Behn, Harling Fellow of the University of Manchester. Communicated by Arthur Schuster, F.R.S. | 444 |

No. A 541.—June 10, 1908.

| | PAGE |
|--|------|
| On the Osmotic Pressure of Compressible Solutions of any Degree of Concentration. Part II.—Cases in which both Solvent and Solute are Volatile. By Alfred W. Porter, B.Sc., Fellow of, and Assistant Professor in, University of London, University College. Communicated by Professor F. T. Trouton, F.R.S. | 457 |
| On Vapour-pressure and Osmotic Pressure of Strong Solutions. By H. L. Callendar, F.R.S., Professor of Physics at the Imperial College of Science and Technology. | 466 |
| Secondary β -rays. By J. A. McClelland, M.A., D.Sc., Professor of Experimental Physics, University College, Dublin. Communicated by Professor J. Joly, F.R.S. | 501 |
| On Scandium. By Sir William Crookes, D.Sc., F.R.S. (Abstract)..... | 516 |
| Note on the Trajectories of Rifled Projectiles with Various Shapes of Head. By A. Mallock, F.R.S..... | 519 |
| Note on the Ascent of Meteorological Balloons and the Temperature of the Upper Air. By A. Mallock, F.R.S. | 530 |
| On the Use of Iridium Crucibles in Chemical Operations. By Sir William Crookes, D.Sc., F.R.S. | 535 |

No. A 542.—June 20, 1908.

| | |
|---|-----|
| On the Measurement of the Atmospheric Electric Potential Gradient and the Earth- air Current. By C. T. R. Wilson, F.R.S..... | 537 |
| On the Hysteresis Loss and other Properties of Iron Alloys under very Small Magnetic Forces. By Professor Ernest Wilson, V. H. Winson, and G. F. O'Dell. Communicated by Sir William H. Preece, K.C.B., F.R.S. | 548 |
| Note on the Representation of the Earth's Surface by Means of Spherical Harmonics of the First Three Degrees. By A. E. H. Love, F.R.S. | 553 |
| The Relation between the Crystalline Form and the Chemical Constitution of the Picryl Derivatives. By George Jerusalem and William Jackson Pope, F.R.S., Professor of Chemistry, Municipal School of Technology, Victoria University of Manchester | 557 |
| A Photographic Determination of the Elements of the Orbits of Jupiter's Satellites. By Bryan Cookson, M.A., Mackinnon Student, July, 1904—July, 1906. Com- municated by H. F. Newall, F.R.S. | 567 |
| Helium and Radio-activity in Rare and Common Minerals. By the Hon. R. J. Strutt, F.R.S. | 572 |
| Effect of a Cross Wind on Rifled Projectiles. By A. Mallock, F.R.S. | 595 |

| | |
|--|-------------|
| | PAGE |
| On the Decay of the Radium Emanation when dissolved in Water. By Richard B. Moore, B.Sc. Communicated by Sir William Ramsay, F.R.S. | 597 |
| Percentage of the Inactive Gases in the Atmosphere : a Correction to Previous Calculations. By Sir William Ramsay, F.R.S. | 599 |
| | |
| OBITUARY NOTICES OF FELLOWS DECEASED | i |
| Index | lxv |



PROCEEDINGS OF
THE ROYAL SOCIETY.

SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCES.

The Annealing of Copper : with Special Reference to Dilatation.

By T. TURNER, M.Sc., A.R.S.M., Professor of Metallurgy, and D. M. LEVY,
A.R.S.M., Assistant Lecturer in Metallurgy, University of Birmingham.

(Communicated by Professor J. H. Poynting, F.R.S. Received May 21,—Read
June 27, 1907.)

It is well known that copper is met with in two distinct forms, viz., the soft state as in cast or annealed metal, and the hard variety which is the result of mechanical work. There is more difference between the mechanical properties of hard and of soft copper than is observed in the case of two distinct metals ; such, for example, as nickel and cobalt.

For instance, one of the most important of these differences, from a practical point of view, is in connection with the tensile strength of the material, which is only about 10 to 14 tons per square inch in cast or in annealed copper, while in hardened copper the tenacity is about twice as great, and usually runs from about 20 to 28 tons per square inch, or even more in special cases. The difference between hard and soft copper can be also readily illustrated by bending two rods about $\frac{1}{4}$ inch square section, one in the hardened and the other in the annealed condition. The latter can be easily bent in the hands or even tied in a knot, while the mechanically worked bar is rigid and elastic, and can only be bent by the application of considerable force. It is common knowledge that hard copper becomes perfectly annealed by heating to 500° C.; that the heating need not be for any lengthened period, and the rate of cooling afterwards is unimportant.

Changes of properties which are so marked, and so far-reaching in the applications of metallic copper, have naturally been the subject of investigation by metallurgists and physicists, among whom may be specially mentioned Roberts-Austen,* Rudeloff,† Thurston,‡ and Heyn.§ These researches deal chiefly with the mechanical properties of copper in various conditions, and at various temperatures.

In addition to the foregoing, reference should be made to the work of Beilby,¶ who has investigated the microstructure of copper in different states: while the expansion of copper, over a considerable range of temperature, was observed by Dittenberger and Gehrke.¶ No particulars are given in their report as to the condition of the metal under examination; but its expansion up to a temperature of 625° C. is stated to be in agreement with the formula

$$\lambda = 10^{-9}(16070 + 4.030 t^2),$$

while a rod 487 mm. long showed a permanent extension of 0.01 to 0.02 mm. on resuming the original temperature.

In the course of an investigation recently conducted at the University of Birmingham on the volume changes during the solidification of cast metals, it was shown that corresponding with each temperature arrest during the cooling of cast iron there was also a definite volume alteration.** It was also shown that copper zinc alloys expand during solidification. For these experiments a simple form of extensometer was employed, and the indications of this instrument show that at certain temperatures, which marked well defined changes in the properties of the solid metal, there were well marked alterations of volume, which were rendered very evident by the extensometer.

It was thought that by the application of somewhat similar methods, information might be obtained as to any abrupt or definite change which may occur when metal, which has been subjected to mechanical work, is, by annealing, converted into the soft variety.

* Roberts-Austen, W., 2nd Report Alloys Research Committee, 'Proc. Inst. Mech. Eng.,' April, 1893, p. 114.

† Rudeloff, M., "Influence of Temperature on Tensile Strength of Metals," 'Mittheil. König. Technische Versuchs-Anstalt,' 1894, vol. 11 (b), pp. 292—330; "Influence of Heat, Chemical Composition and Mechanical Treatment on Strength and Ductility of Copper," 'Mittheil. König. Technische Versuchs-Anstalt,' 1898, vol. 16 (a), pp. 171—219.

‡ Thurston, 'Materials of Engineering,' Part III, pp. 477—573.

§ Heyn, E., "Overheating of Mild Steel" (refers to copper), 'Journ. Iron and Steel Inst.,' 1902, vol. 2, p. 101.

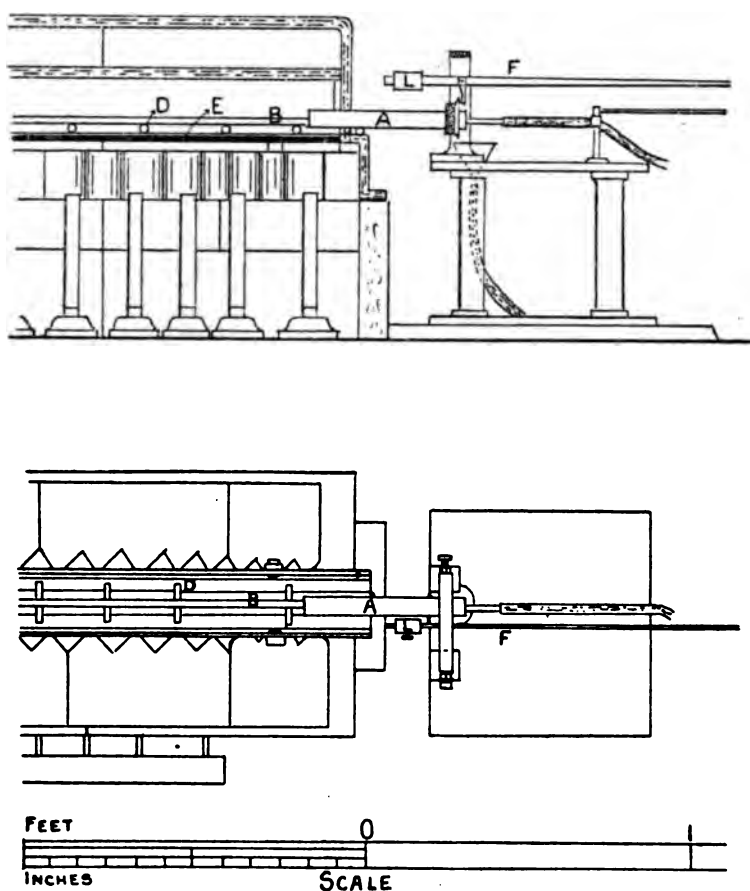
¶ Beilby, G., 'Journ. Soc. Chem. Ind.,' 1903, pp. 1107—8; 1904, p. 788.

¶ Report of Physikalisch-Technische Reichsanstalt, by Holborn and Grüneisen, 1902, abstracted in 'Engineering,' vol. 4, No. 24.

** T. Turner, "Volume and Temperature Changes during the Cooling of Cast Iron," 'Journal of the Iron and Steel Institute,' 1906, vol. 1, p. 48.

In order to make the desired observations an extensometer was devised capable of indicating the changes of length of a bar of copper at temperatures from that of the atmosphere to about 700° C. At the same time the temperature of the bar was ascertained by a pyrometer of the Le Chatelier thermo-junction type.

The general arrangement of the apparatus is shown in fig. 1; whilst fig. 2 represents, on a larger scale, details of the method of connecting with the extensometer.



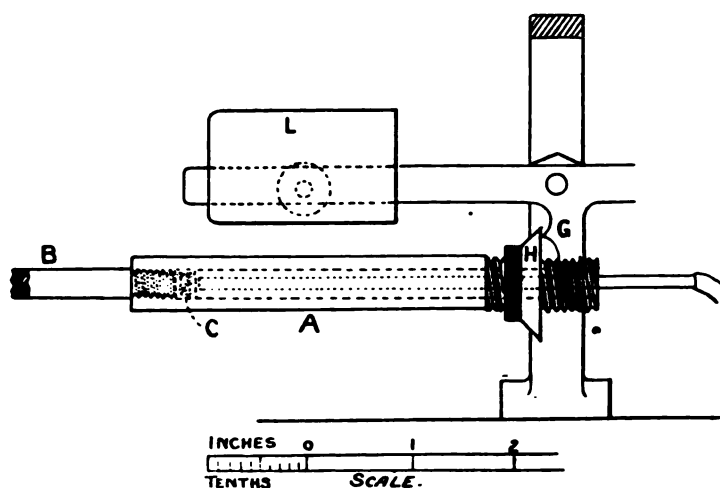
ARRANGEMENT OF APPARATUS FOR MEASURING DILATATION.

FIG. 1.

Numerous forms of apparatus were tried before the final design was adopted, as it was essential to heat the bar uniformly and to ensure that the expansion of the whole length and of that alone should be recorded, the difficulty being

to connect the bar, which was of considerable length and entirely in the furnace, with the extensometer, which was situated at some little distance away.

The bars used in the series of experiments were all $\frac{1}{4}$ inch in square section and 35 inches long. Each bar (B) was heated in a gas fired tube furnace as subsequently described; and, in order to confine the rise of temperature to the bars, they were fitted at each end with a copper tube (A) 4 inches in length. This tube was screwed on to the bar for a distance of about $\frac{1}{2}$ inch, and projected about 3 inches beyond the end of the furnace. The bar itself was thus entirely in the furnace, and in order to prevent the expansion of the connecting tubes being recorded they were water cooled, while the end of



DETAILS OF EXTENSOMETER CONNECTION.

FIG. 2.

the bar inside the tube was covered with an asbestos plug (c) so as to prevent the water having any cooling effect in it. One of these copper tubes was firmly clamped so as to be kept quite rigid, while to the tube at the other end the extensometer was attached. In this way the expansion of the whole length of the bar was obtained, while the rest of the system was maintained at a constant temperature.

In order to allow freedom of motion in the direction of its length, the rod rested on a number of small porcelain rollers (D) which were supported on a trough made of steel bars, $\frac{1}{4}$ inch thick and 3 inches wide. The trough is open at both ends, and in order to prevent buckling effects due to the heat it was well braced, whilst the rollers, instead of running directly on the bottom

of the trough, were supported by two thin strips of steel. In the earlier experiments with a thinner trough, there was sufficient buckling to seriously affect the observations.

The trough was heated by a series of bunsen burners, controlled by a common tap, and so placed as to ensure, as nearly as possible, uniformity of heating. It is known that tube furnaces are usually cooler at the ends than in the middle, and pyrometric tests were made throughout the trough in order to determine the proper number and spacing of the gas burners. By surrounding the trough with brickwork, covering the ends and top with asbestos cardboard, and providing a considerable covered air space around the trough, it was ultimately found possible to ensure very considerable uniformity of temperature throughout the tube.

The extensometer consisted essentially of a bell crank lever (F) mounted on pivots; the indicating arm was 25 inches long, whilst the short arm was so fashioned that at a distance of $\frac{1}{2}$ inch from the pivots it took the form of a finely rounded projection (G). This pressed against a brightly polished disc (H) screwed on to one of the connecting tubes, by means of which the forward motion of the disc (*i.e.*, the expansion of the rod) was indicated on a scale (K), which was an arc of a circle divided in millimetres.

The extensometer worked in a vertical plane, and was very delicately mounted so as to reduce the effects of friction to a minimum. On being tested by a micrometer screw its indications were found to be fairly uniform in all positions, and the millimetre scale denoted a magnification of 48; in other words, 1 mm. scale-division corresponded to an expansion of $1/1200$ of an inch. The indicating arm was extended backwards for some distance beyond the pivots, so as to accommodate a balance weight (L), which was, however, placed at such a distance as to always insure a small positive pressure against the brass disc in whatever position the indicator arm might happen to be situated. As the copper connecting tube at the other end was firmly clamped, it was only necessary to take the extensometer readings from one end in order to measure the expansion.

The extensometer was made in the Metallurgical Department of the University of Birmingham, by Mr. J. Ward, the University steel melter, and the authors desire here to acknowledge the value of the assistance thus rendered by Mr. Ward.

The temperatures were recorded by a thermocouple, the junction (M) being placed in an $\frac{1}{8}$ -inch hole bored in the centre of the bar under examination. The leads from the cold junction were connected with a dead-beat galvanometer of the D'Arsonval type, in the mirror of which the

reflections of a graduated scale were observed through a telescope placed some distance away.

The adjustments of the apparatus required careful attention, and the precautions detailed in the foregoing paragraphs were adopted as the result of a very large number of experiments at the commencement of the work. These tests showed that minute frictional effects, slight draughts, and other very small deviations led to irregularity in the results obtained.

The quantity of asbestos used as a non-conducting plug at the end of the rod, the use of steel strips for the rollers to run upon, the adoption of movable bunsens instead of the usual form of combustion furnace, and the careful adjustment of the counter-balance on the extensometer were all decided on after a number of early failures. More uniform results were obtained when the junction was inserted in a hole in the metal instead of fastening it on the surface, whilst the exclusion of draughts by employing brickwork and asbestos protection was most important. Marked effects were also produced by any irregularity in the supply of cooling water to the ends of the rod, and it was considered advisable to run the water under a constant head from a fixed reservoir some feet above the level of the apparatus. The actual operations were conducted as follows.

The adjustments of the apparatus being made so that the indicator was near, but not at the bottom of the scale, the clamps were made tight, and a gentle stream of water was set flowing through the connecting tubes for some minutes, zero readings were noted, the bunsens were then lighted at the full, and observations taken of the indicator and the galvanometer at intervals of 15 seconds.

The changes, which were at first rapid, become gradually smaller, and after a red heat had been attained, half-minute, then one-minute, and finally two-minute intervals were allowed between the readings until the maximum temperature had been reached, at which point the readings had become practically constant. The gas was then turned off, and readings were taken during the cooling of the bar. The results were then plotted so as to give a continuous record of the changes of length and of the increments of temperature.

Preliminary Experiments.

The first series of experiments was undertaken in order to test the delicacy of the apparatus and the trustworthiness of the method. The object was to ascertain whether, when a material was employed which is known to undergo abrupt changes of length at certain critical points, these changes could be readily and accurately observed, and, secondly, to determine

whether, in the case of a material which undergoes no such abrupt changes, a perfectly continuous curve could be obtained.

The materials which suggested themselves as being most suitable for the above purposes were steel and wrought iron, as it is well known that with high carbon steel there is an abrupt change of volume at about 680°C ., while no such change takes place with wrought iron. The change in volume in the case of steel is known to be connected with the state of combination of the carbon which is present, and this volume change is accompanied by marked differences in hardness and other properties.

The wrought-iron bars used for these tests were of best Staffordshire iron, and contained 0.03 per cent. of carbon. The steel was made in the Siemens furnace, and contained 0.94 per cent. of carbon. The bars were, as before described, 35 inches long, $\frac{1}{4}$ inch square section, and the experiments were all conducted exactly as previously mentioned.

(a) *Wrought Iron*.—The curves obtained from heating and cooling a bar of wrought iron are shown on fig. 3. From these it will be seen that within the range of temperature employed the curves are regular and continuous, and the absence of any break or arrest may be taken to indicate that the apparatus was satisfactory, and that the precautions previously mentioned had eliminated all important sources of error.

(b) *Steel*.—The curves obtained from the steel with 0.94 per cent. of carbon are also given in fig. 3, and these indicate that a marked diminution in length occurs at the temperature arrest point, A_{r1} , which corresponds with about 680°C . On cooling the bar a corresponding increase of length occurs at the same temperature.

M. H. le Chatelier* has already, by an entirely different method, determined the expansions of iron and steel at various temperatures, and the results of the present experiments given above are in practical agreement with his observations. Messrs. Charpy and Grenet† have also studied the transformations of steel by the dilatometric method, using the method of Le Chatelier. These observers point out that in order to obtain satisfactory numerical values it is necessary to heat at a sufficiently slow speed, and state that about 200° per hour is a suitable increment, a rate which does not differ very markedly from that adopted in the present series of experiments. Charpy and Grenet also found that in all steels, and cast iron containing only carbon, the transformation took place at about 700°C .; that with low carbon steels the contraction at this temperature was inappreciable; and that the

* 'L'Etude des Alliages,' Paris, 1901, p. 403.

† 'The Metallographist,' 1903, p. 240; 'Comptes Rendus Académie des Sciences,' May 10, 1902.

maximum contraction was observed in steels which contained 0.93 per cent. of carbon.

As the curves obtained both for iron and steel by the extensometer apparatus agreed with those of previous experimenters, alike in the character and extent of the changes which take place, and the temperature at which any irregularity is noted, it may be assumed that the accuracy and suitability of the method of investigation was sufficiently proved. It was therefore possible, with confidence, to approach the real object of the research.

Dilatation of Hard-drawn Copper.

The rods used in these tests correspond in every way with those employed in the tests for iron and steel, being 35 inches long, a $\frac{1}{4}$ inch in square section, and screwed to water-cooled copper connecting-tubes as before. The rods were supplied by Messrs. Thos. Bolton and Sons, of Oakamoor, Staffs, and were of electrolytic copper of selected quality and uniformity. They had been rolled while hot down to $\frac{3}{8}$ inch square, and were afterwards cold drawn until $\frac{1}{4}$ inch square. The curve obtained on heating a bar of this hard-drawn copper to about 500° C. is given in fig. 4. At this temperature the metal is completely annealed, and, on cooling, is dead soft. It will be observed that both the heating and cooling curves are quite regular, there being no break such as would be caused by the slightest abrupt change of volume at a critical temperature. There was nothing observed which would serve to indicate at exactly what temperature hard copper passes into the soft variety. As a check upon the results obtained by the extensometer, the rod was marked before being placed in the furnace, a length of 30 inches being taken, and when the metal was cold, after the conclusion of the experiment, there was no perceptible alteration of length in the marked portion.

Dilatation of Annealed Copper.

The annealed rod, as used in the previous experiments, was now heated to about 600° C., and afterwards allowed to cool slowly to the temperature of the atmosphere. From the curves obtained (fig. 4) it will be observed that the dilatation was as regular as with wrought iron, and quite similar to what was observed with the hard-drawn copper. It thus appears that the change from the hard elastic condition of worked copper to that of extremely soft metal, such as is obtained with fully annealed copper, is not accompanied by any alteration of length. It may be recalled that it is usual to make allowances in practice for the volume changes which accompany the cooling of cast iron or the hardening of steel: while we are informed, by Mr. F. Platten, of

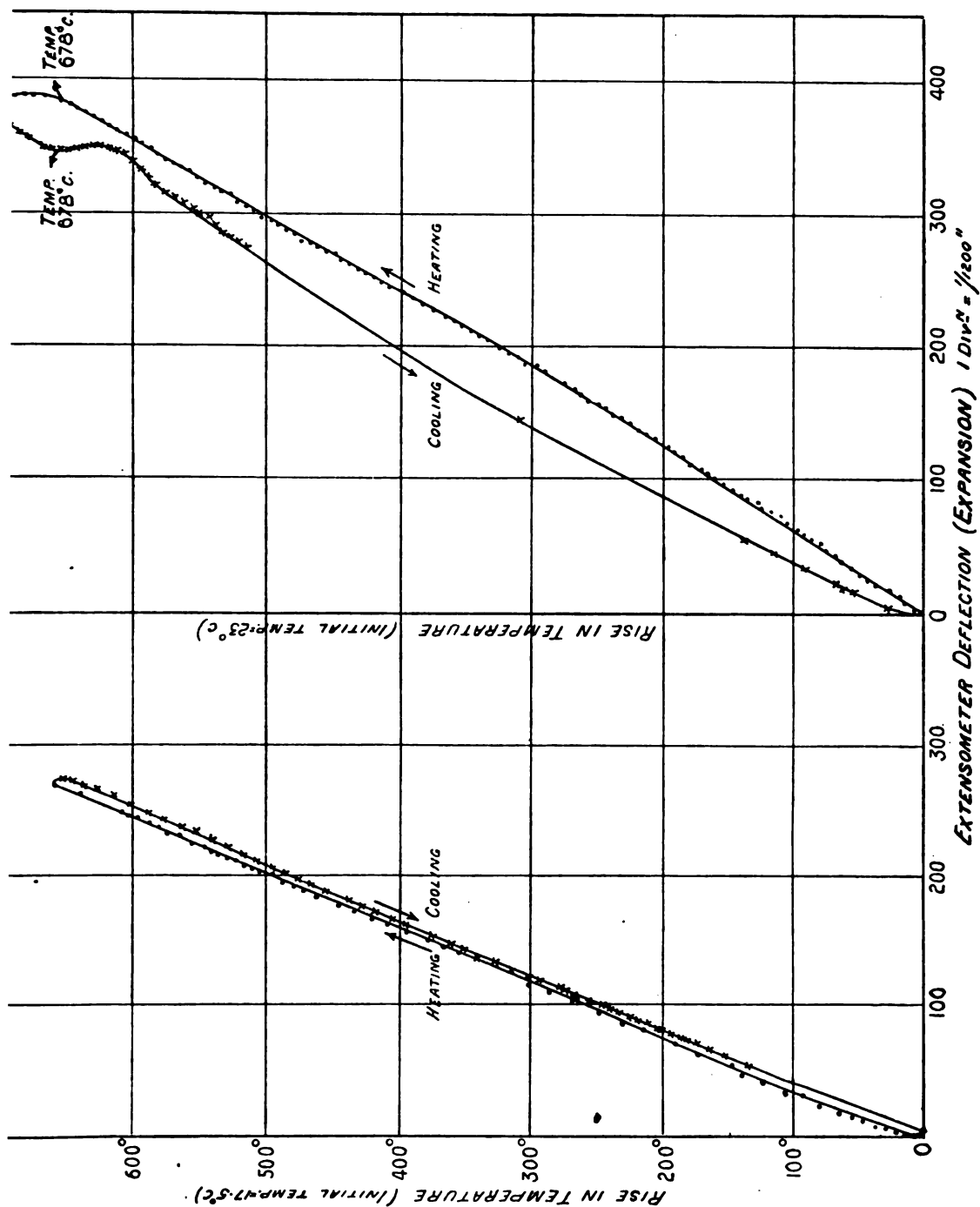
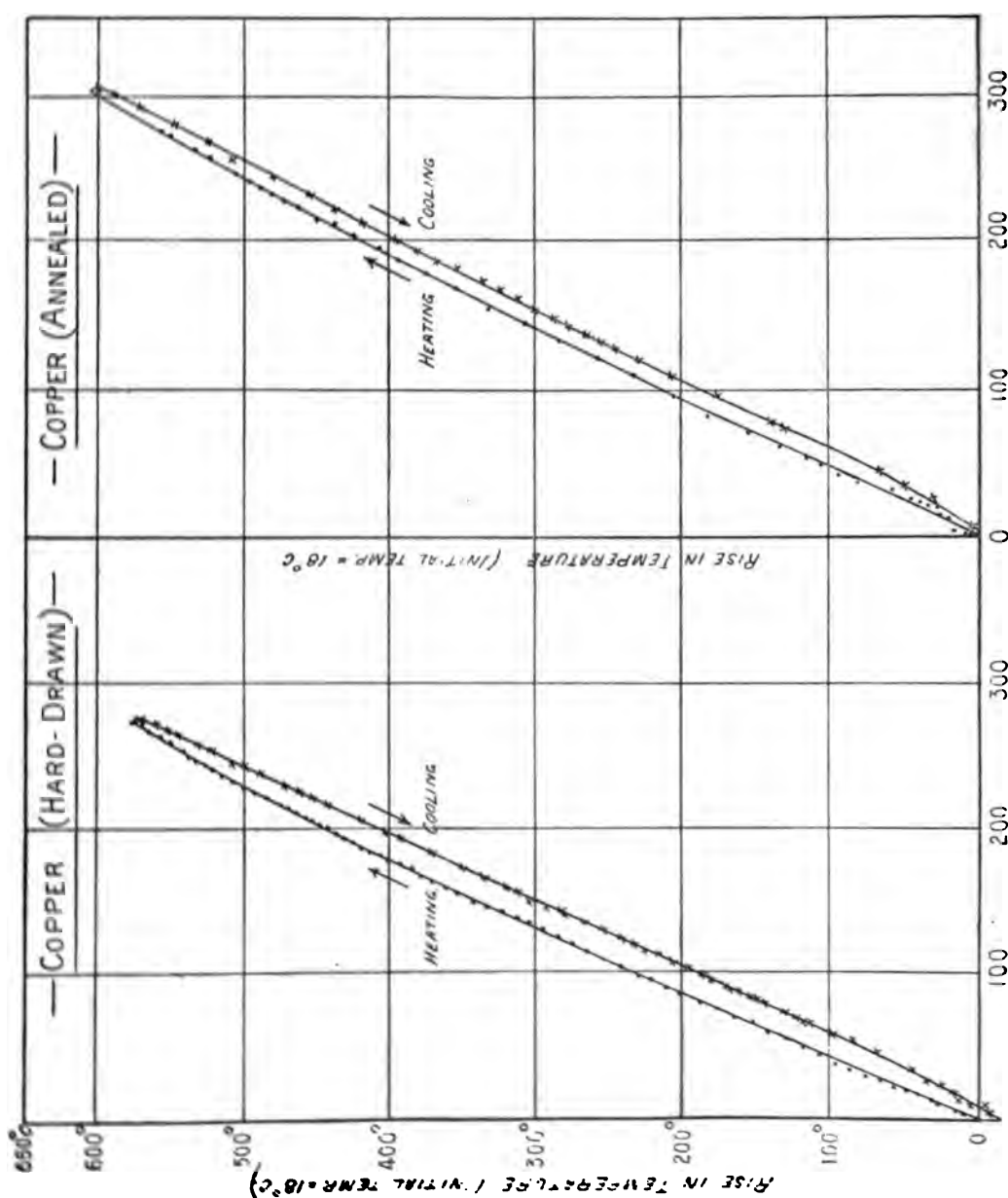


FIG. 3.



Elliott's Metal Company, Limited, that, on the other hand, no allowance is made, when annealing hard copper in the processes of rolling or drawing, for any alterations in length or thickness.

Dilatation of Copper Alloys.

It was now considered advisable to examine certain well-known copper alloys which are of commercial importance ; which are hardened by work, and which may be annealed at a relatively low temperature like copper itself. For this purpose Mr. Platten kindly supplied hard-drawn $\frac{1}{4}$ -inch-square rods having the following composition :—

- | | |
|-------------------------------|---------------------|
| 1. Brass (copper 70, zinc 30) | 4. Gun metal. |
| 2. „ („ 66, „ 34) | 5. Phosphor bronze. |
| 3. „ („ 60, „ 40) | |

These were examined in 35-inch lengths exactly as in the previous experiments, and the results plotted. No satisfactory curve was obtained of the 60:40 brass as all the rods of this composition which were tested behaved in a curious manner, showing a normal expansion up to a certain point and then beginning to develop a helical twist which rendered it impossible to obtain any trustworthy indications with the extensometer, as the bars were no longer straight. The other four alloys, namely 70:30 brass ; 66:34 brass, gunmetal, and phosphor bronze gave perfectly regular and uniform curves as the temperature rose, and no indication was afforded as to the point at which the hard metal became annealed. The cooling curves were all quite regular, and similar to each other, though the contraction was very slightly more rapid above 400° and slightly less rapid below 400° than might have been expected from the heating curve.

The conclusion to be drawn from these experiments would appear to be that the alterations which take place when hard copper is by annealing converted into the soft variety are unaccompanied by any change in linear dimensions. It is known that the separation of a constituent, as of graphite from cast iron or pearlite from steel, is accompanied by marked dilatometric changes. Le Chatelier* has shown that a dimorphic transformation such as that which ferrous sulphide undergoes between 100° and 150°, is accompanied by a marked change of volume. Allotropic changes in an element are also usually accompanied by marked alterations of volume, as in the case of pure iron at about 880° C. It is evident, therefore, that such changes in the properties of copper and of copper alloys as are caused by mechanical work or

* 'Metallographist,' 1903, p. 23 ; 'Bulletin de la Société d'Encouragement,' September, 1902.

annealing respectively are of a different order to those which are due to allotropic or dimorphic transformations, or to the separation or rearrangement of constituents. The results here recorded lead us to believe that mechanical work produces only internal rearrangement of the metallic grains or molecules, but does not lead to any chemical or physical changes such as are correctly regarded as allotropic. We have met with no evidence to support the view that allotropic change results from mechanical work.

A New Current Weigher, and a Determination of the Electromotive Force of the Normal Weston Cadmium Cell.

By Professor W. E. AYRTON, F.R.S., and T. MATHER, F.R.S., Central Technical College, London, and F. E. SMITH, A.R.C.S., National Physical Laboratory, Teddington.

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(Abstract.)

Introductory.

The instrument described is the outcome of conversations between the late Professor J. Viriamu Jones, F.R.S., and one of the authors (W. E. A.), on their return from the British Association Meeting held in Toronto in 1897. Its object was to determine "the ampere" as defined in the C.G.S. system, to an accuracy comparable with that attained in the absolute determination of the ohm by Lorenz's apparatus, an account of which was given by Professors Ayrton and Jones at the Toronto Meeting.*

Professor Jones had previously developed a convenient formula for calculating the electromagnetic force between a helical current and a coaxial current sheet, viz.,

$$F = \gamma_A \gamma (M_2 - M_1), \dagger$$

where γ_A is the current in the helix, γ the current per unit length of the current sheet, and M_1, M_2 the coefficients of mutual induction of the helix and the two ends of the current sheet respectively. By using coaxial coils with single layers of wire wound in screw-thread grooves, advantage could be taken of the above formula.

* See 'B. A. Report,' Toronto, 1897, p. 212.

† 'Roy. Soc. Proc.,' vol. 63, p. 204.

A preliminary apparatus was made at the Central Technical College in 1897-8, and used to obtain experience as to the conditions necessary for successful operation.* The design of the proposed instrument was then proceeded with.

By employing the arrangement devised by one of the authors (W. E. A.), of having double-threaded screw grooves wound with separate bare wires subsequently connected in series, it was possible to prevent any uncertainty existing regarding leakage between adjacent turns of a spiral. At the same time, the absence of any silk covering on the wires wound on bare marble cylinders enabled very great precision in the measurement of the dimensions of each coil to be attained.

Complete working drawings and specifications of the proposed instrument and its adjustable support were prepared at the Central Technical College in 1898-99, Mr. J. P. Gregory, a then student of the College, rendering very valuable assistance in this work. Grants amounting to £300, for the construction of the balance, were made by the British Association for the Advancement of Science in 1897 and 1898, and Sir Andrew Noble, F.R.S., kindly presented the adjustable phosphor bronze stand, designed to support the instrument. The physical balance was built by Mr. L. Oertling, of London; and the electrical portions were made at the National Physical Laboratory under the supervision of the Director, Dr. R. T. Glazebrook, F.R.S.

General Description.

The instrument consists of a very sensitive physical balance, with a 20-inch beam,† supporting from each end a coil with vertical axis; these coils hang coaxially within fixed coils carried from the base. All the coils are wound in single layers on hollow marble cylinders having *double-threaded* screw grooves cut on their surfaces, the fixed cylinders being about 13 inches diameter, 11 inches high, and 2 inches thick, and the suspended cylinders $8 \times 6 \times \frac{1}{2}$ inches. Each fixed cylinder carries two windings, an upper and a lower, in which the current circulates in opposite directions, so that one repels and the other attracts, the current carrying winding on the suspended cylinder hanging symmetrically between them. Each winding, on both fixed and suspended cylinders, consists of two helices occupying adjacent grooves of the double-threaded screws; there are thus 12 wires in all on the four cylinders, and these are connected all in series in the ordinary use of the balance.

Connection with the suspended coils is made by flexible silver wires 1 mil

* 'B. A. Report,' Bristol, 1898, p. 157; also 'Journ. Inst. Elec. Engrs.,' vol. 35, p. 12.

† The balance carries about $5\frac{1}{2}$ kilos, and turns with 1/10 milligramme.

in diameter, arranged 80 in parallel, and all other leads to and from the coils are of small concentric cable. These cables run to a plug board and commutators, whereby the current in any or all of the 12 helices may be reversed. Adjacent helices can also be disconnected from each other, and electrically grouped so that the insulation between all the pairs may be found by a single test.

When in use for measuring current, the directions of circulation in the several coils are arranged so that they all produce a torque in the same sense on the balance beam, and this torque is balanced by suitable masses placed on the scale pans. Reversal of the current, in the fixed coils only, produces an apparent change of weight, which is a measure of the square of the current employed. The position of the beam of the balance is observed by viewing through a microscope a finely divided scale carried by the pointer.

The masses used to balance the electromagnetic forces can be manipulated quickly and conveniently without opening the case of the instrument, four weight lifters being provided for this purpose. To prevent change of level of the suspended cylinders on removing or replacing the weights, the scale pans are carried on separate planes resting on the knife edges from which the suspended coils hang.

For convenience in erection and adjustment the fixed coils are supported on phosphor bronze slide rests, capable of about half an inch movement in two horizontal directions and of 14 inches vertical displacement.

Advantages of Duplication of Coils.

The arrangement of having a set of coils at each end of the balance beam has several advantages. Independent determinations may be made on the two sets, or, by using both together, the forces are approximately doubled. Differential tests can also be made so that one set serves as a check on the other. The chief advantage, however, is the symmetry obtained, which neutralises to a very great extent the disturbances arising from convection currents of air and change of air buoyancy.

The double winding is also of great utility in this respect, as it permits of an electromagnetic weighing being made with one set of coils without introducing the error, due to drift of zero, which would occur if that set alone were heated by the passage of the current. This is effected by arranging the connections so that the currents in adjacent helices on one pair of cylinders are in opposite directions; they have then no electromagnetic effect, and yet are heated by the passage of the current just as much as the coils on the other pair.

Magnetic Tests.

Before constructing the parts of the balance, magnetic tests were made on all the materials intended to be used, and in cases where the permeability differed appreciably from unity those parts were rejected.

When the instrument was completed it was used to test itself, but no trace whatever of magnetism could be detected.

Construction and Winding.

The material employed for the fixed and suspended cylinders is Carrara Statuary Marble, which, after being turned approximately to size, was baked in an oven at 140° C. for 30 hours and then immersed in hot paraffin wax. The turning was then completed, the V grooves cut and bare copper wire, No. 24 S.W.G., wound in them under tension, numerous measurements of the diameter of the wire being made during the winding. Special arrangements were made to ensure that each helix contained an exact number of turns, and that the two helices of one pair start and end in the same diametral plane.

The pitch of the screw grooves is $1/18$ inch: each helix on a suspended cylinder has 92 turns, making 184 in all, and those on each fixed cylinder 90 turns, making a total of 360. These turns on the fixed cylinders are in two portions, upper and lower, with an unwound space of $2/18$ inch between them. The axial length of the suspended coil is, therefore, equal to the distance between the central planes of the upper and lower windings on the fixed cylinder. On all the cylinders the total number of turns is 1088 and the total length of wire about 980 metres.

Measurement of Coils.

Measurements of the axial lengths of the windings were made by a cathetometer, and of the diameters by a special measuring machine obtained from Messrs. Stanley, of London. An optical lever used with the latter instrument gave a deflexion of 2 mm. for a movement of the micrometer of 1μ ($1/1000$ of a millimetre), so the dimensions could be determined with great precision. Such accuracy in the measurement of the diameters was rendered possible owing to the use of bare wire wound on bare marble.

About 120 diameters were measured on each suspended cylinder, and about 220 on each fixed one, the probable error of the mean diameter of any cylinder amounting to about five in a million. All the cylinders are very nearly perfect, the ellipticities and the conicalities being extremely small.

After measuring the coils and insulating adjacent helices, the windings were coated with melted wax, and again measured in numerous places from which the wax was temporarily removed; no appreciable change in dimensions could be found.

Erection and Adjustment.

To facilitate the setting of the cylinders, two spirit-levels are mounted on the upper plane end of each, and adjusted so that when these indicate level the axis of the corresponding cylinder is truly vertical. Mechanical indicators are also provided for showing when the cylinders are co-axial and when the middle planes of the windings on the fixed and suspended cylinders coincide. The vertical and horizontal adjustments can also be tested by electrical methods which are simple and very accurate; these were adopted in the final settings, the error introduced by faulty adjustment amounting to something less than 1 part in 5 millions.

Calculation of Mutual Inductions and Forces between the Coils.

The formulæ employed are given in Professor J. V. Jones' paper, mentioned on p. 12, and were employed by two of the authors (T. M. and F. E. S.) to calculate *independently* the mutual inductions and the forces between the fixed and suspended coils when a current of 1 ampere circulates in them. The values of $M_2 - M_1$, defined on p. 12, calculated (a) with logarithms and (b) by calculating machine, were in very close agreement, the difference being less than 1 in a million. The actual numbers are 25962.02 cm. and 25962.04 cm. respectively for the left-hand set of coils, and 25960.45 cm. and 25960.43 cm. for the right-hand set. This order of accuracy in the values of the coefficients of mutual induction is rendered quite real by a knowledge of the exact position of the bare conductors and the certainty that no current leaks from one convolution of wire to any other. In both cases the sum for both sets of coils is 51922.47 cm., and this number was used in most of the determinations.

Taking the value of g , the acceleration of gravity at Bushy, as 981.20, and the length of winding on the suspended cylinders as 12.9830 cm., the change of apparent mass on reversal of 1 ampere in both sets of coils becomes

$$m = 14.9992, \text{ grammes.}$$

This assumes that no forces exist between the fixed coils on one side of the balance and the suspended ones on the other side. As a matter of fact, such forces are present, but can be eliminated by taking two sets of readings, one set in which the cross actions assist the direct ones and the other set in which

these forces oppose each other. These sets give what we have called (D + S) (direct + secondary) and (D - S) observations respectively. The change from one condition to the other is effected by simply reversing the direction of current in all the coils on one side of the balance; this leaves the direct forces unchanged in direction but reverses the secondary forces.

In the majority of the determinations (D + S) and (D - S) observations were taken in succession and the current calculated from the expression

$$\text{amperes} = \sqrt{(m'/29.99856)},$$

where m' is the sum of the balancing masses in the (D + S) and (D - S) tests.

Tests on Cadmium Cells.

To determine the E.M.F. of a cell, an electric current supplied by a 110-volt storage battery was passed through a standard resistance of approximately 1 ohm, in series with the current weigher, and adjusted in strength until the P.D. between the terminals of the resistance balanced the E.M.F. of the cell. The magnitude of this current was then determined by the instrument, the cell and the resistance being kept at very nearly constant temperature during the measurements. Switches with copper contacts and terminals, to minimise thermal E.M.F.'s, were used in the cell circuit, and reversals of current and of the cell were sometimes made to eliminate inaccuracies which might otherwise be introduced by such E.M.F.'s.

As the steadiness of the balance was much greater when the instrument was cold than when heated by the long continued flow of the current in the coils, our usual procedure was to make one complete set of observations, (D + S) and (D - S), in the morning and another in the afternoon. The interval between the morning and afternoon readings was often devoted to silver deposit determinations, the combination of cell and standard resistance being used as a secondary standard of current during the depositions. An account of work on silver is well advanced, and will be published shortly.

In all some 71 observations have been made on a certain cadmium cell (N.P.L., No. 2), using both sets of coils on the balance, and 13 observations in which one or other of the two sets was employed. The agreement between the individual results obtained with the two sets of coils is remarkable, the average difference from the mean amounting to only six parts in a million. The whole series of observations extended over a period of 19 months (September, 1905, to April, 1907), and during that interval the coils of the balance were reset five times. No determination made has been omitted, except those in which the observations were of such a nature that

a decision to disregard the result was arrived at before its computation. Such occasions were very rare.

Of the 71 observations made, 7 are within 1 in a million of the mean, 14 are within 2, 28 within 5, 53 within 10, 66 within 15, and 70 within 20 in a million.

Only 1 determination out of the whole 71, and this one of the earliest, differs from the mean by so much as 1 part in 59,000.

The above facts constitute important evidence of constancy in both cell and balance. In fact, both current weigher and cell proved to be much more constant and trustworthy than the standard resistance, although the latter was very carefully made and annealed with a view to ensuring permanency.

Expressed in terms of the international ohm, as realised at the National Physical Laboratory, and of the ampere as given by the new current weigher, the value of $C \times R$ for the normal Weston cadmium cell is

$$1.01830, \text{ at } 17^\circ \text{ C.}$$

This assumes that the value of g at Bushy is 981.19, a number probably correct to within 3 parts in 100,000. An uncertainty of this amount in g introduces a possible error of $1\frac{1}{2}$ parts in 100,000 in the value of the ampere, and, as all other probable errors are smaller in magnitude, it is important that a more accurate determination of g at Bushy should be made.

To realise the volt with an accuracy approaching that of the ampere as now known, it is necessary that an absolute determination of resistance of corresponding precision be undertaken. At the present time the uncertainty in the absolute value of the international ohm approximates to 4 parts in 10,000.

From the above value of $C \times R$ for the cadmium cell, together with the ratio of Clark to cadmium, viz. —

$$\text{Clark at } 15^\circ \text{ C.} \div \text{cadmium at } 17^\circ \text{ C.} = 1.406,$$

the E.M.F. of the Clark cell at 15° becomes

$$1.432,$$

Two Appendices accompany the paper: one of these gives the numerical values of the constants in the series for calculating F and E , the complete elliptic integrals of the first and second kinds respectively: the other relates to the corrections in the forces between the coils of the balance arising from the finite thickness of the wire used, and from the fact that helices are substituted for current sheets. Neither of these corrections affects the results appreciably.

Some historical notes are given in the paper.

On Luminous Efficiency and the Mechanical Equivalent of Light.

By CHARLES V. DRYSDALE, D.Sc.

(Communicated by Silvanus P. Thompson, D.Sc., F.R.S. Received June 8, 1907.)

(Abstract.)

The determination of the efficiency of various forms of illuminants, and of the power expended in light production, does not appear to have received the attention it deserves in this country, nor have the labours of workers in Germany and in the United States as yet sufficed to permit of definite values being adopted for luminous efficiencies, or for the mechanical equivalent of light. In what follows, an account of some observations made by Mr. A. C. Jolley and the writer, with the object of determining the mechanical equivalent of light, will be given. For this purpose an attempt was first made to find the luminous efficiencies and total consumption of some of the newer highly incandescent electric lamps; and this was followed by a direct determination by a bolometer in the spectrum.

I. *Luminous Efficiency.*

Let Q be the total power consumption of a source.

R the "total radiation" $= \int_0^\infty I_\lambda d\lambda$, the remaining power, $Q - R$ being dissipated by conduction or convection.

L the "luminous radiation" $= \int_{\lambda_1}^{\lambda_2} I_\lambda d\lambda$, where λ_1 and λ_2 are the limits of the visible spectrum, say, 0.39μ and 0.76μ , respectively.

L_λ the "equivalent luminous radiation" $= \int_0^\infty \kappa_\lambda I_\lambda d\lambda$, where κ_λ is a factor which is proportional to the luminosity and taken to be unity for a wave-length of 0.54μ , which is that of maximum luminous utilisation of energy.

Then the "luminous efficiency" in its ordinary acceptation is $\eta = L/Q$. This is the quantity which is called by Nichols* the "total efficiency." Methods which take no account of conduction or convection losses seek to determine the ratio $\eta_r = L/R$, which Nichols terms the "radiant efficiency." Lastly, a suggestion of Dr. Guillaume's† leads to a new definition, $\eta_\lambda = L_\lambda/Q$, which might be termed the "reduced luminous efficiency," as it is reduced in terms of the standard monochromatic light. It is obvious that while

* 'Phys. Rev.,' vol. 17, p. 267.

† 'Soc. Int. Elec.,' Bull. V, pp. 363-400.

with the ordinary definition a source would have unit efficiency if $L = Q$, or the whole of the energy were within the spectrum, and might yet be a very ineffective source as an illuminant if its radiation were confined to near the ends of the visible spectrum; Dr. Guilleaume's definition would only lead to unit efficiency in the case of a monochromatic source of wave-length 0.54μ .

II. *Measurement of the Mechanical Equivalent of Light.*

The most direct mode of procedure is obviously to allow a beam of light of any required quality to fall simultaneously on some form of radiometer and a photometer; and to compare the indication of the radiometer with that obtained from a known source of radiation at a given distance. As nearly all devices for measuring low intensities of radiation are liable to troublesome variations, it is of the greatest importance that the comparison between the radiation in the beam under test, and the known radiation, should be effected as quickly and easily as possible, and with the minimum of disturbance.

Fig. 1 shows the arrangement of apparatus adopted after consideration of the above points. A small intense source of light such as an arc or Nernst filament was employed, in conjunction with a lens, L, and carbon bisulphide prism, P, to form an approximately pure spectrum at the photometer and radiometer box, B. By using a narrow slit an approximately monochromatic light of any required wave-length could be projected on to the photometer, while by widening the slit a band of any width up to the entire limits of the visible spectrum could be employed, the integration being automatically performed without any other collecting device. The known source of radiation consisted of a glow lamp which will be referred to as the "comparison lamp," C.L., placed close to the prism (in some cases beneath it, so that both were approximately on the axis of the bench). A standard glow lamp, S.L., was kept continuously burning on the other side of the photometer box, B. A fixed screen, S, with an aperture, served to block off all radiation but that from the prism, P, or comparison lamp, C.L., while a sliding metal screen, S', actuated by a cord, could be rapidly moved in front of one or the other. In taking the readings the light from the prism was allowed to fall on the bolometer, and the current through the comparison lamp varied until on moving the screen, S', in front of P or C.L. alternately, no change could be noticed. In this way all disturbances due to external changes of temperature could be eliminated, and the observations were much more rapidly obtained than by waiting for slow deflections.

A glow lamp was used as the standard source of radiation for the following

reasons: (a) The total power is easily measured by the P.D. and current, and can be readily regulated; (b) the ratio of convection and conduction to radiation is very small, owing to the high temperature of the filament. These advantages render the glow lamp immeasurably superior to low temperature sources such as employed by Thomsen and others. On the other hand the radiation is not uniformly distributed. But this difficulty can be overcome by determining once for all the relation of the intensity in any given direction to the mean spherical emission, and this may conveniently be determined photometrically.

The photometer employed was of a special form devised by the writer for ordinary and heterochromatic measurement. It consists simply of two totally reflecting right-angled prisms, mounted with their edges in contact. When this combination is set up between two lamps, the light from each is reflected forwards, and can be received on a screen placed in contact with the front face of the prism. This screen may be simply of translucent paper, or opal glass, in which case the appearance is identical with that of the Joly paraffin block photometer; or in the form of a discrimination diagram which serves for heterochromatic work. This diagram is made up of letters and reticulations of different sizes, and both on light and dark backgrounds, the letters and designs being absolutely symmetrical. The advantages of this arrangement are, briefly, that it serves either for isochromatic or heterochromatic photometry; it is absolutely symmetrical; it is not affected as are the wedge photometers by a slight inclination to the axis of the photometer bench; it forms a very sensitive cross staff for indicating whether the lamps and the photometer are in line, and whether there is any inclination to the axis; and, lastly, it permits any portion of a spectrum to be brought exactly to the dividing line so that the comparison may be made with a fairly short spectrum on one side.

For the measurement of the energy a pair of thermo-junctions on the lines employed by Professor Féry* was at first made up, but was found insufficiently sensitive. They were therefore replaced by a bolometer, which was made of 50 cm. of 2-mil copper wire wound backwards and forwards on a mica frame, and had a resistance of about 7.5 ohms. Two such bolometers were made and mounted in the same case with the photometer prisms, the centre of the bolometer being carefully adjusted to be over the edge of the prisms so as to be in the part of the spectrum under photometric examination. To protect the bolometers from draughts the two ends of the box and the observing window were covered with quarter-wave mica sheets. The two bolometers were separated by an asbestos screen, and

* "Rayonnement Calorique et Lumineux," Thèses, Paris, Série A, No. 1111.

were connected to three terminals on the top of the box, from whence three flexible conductors were taken to a Carey-Foster bridge. By having the two bolometers, changes of the air temperature are of less importance, and the whole photometric and radiometric arrangement is reversible. The ratio coils were of 10 ohms each, and a moving coil galvanometer having a resistance of 7.5 ohms and a sensitiveness of 22 mm. per microvolt was employed. The current in each of the bolometer grids was from 0.04 to 0.1 ampère.

In taking the readings the photometer head was first fixed in the middle of the bench, and the spectrum moved until the required colour appeared at the dividing edge between the prisms. The standard lamp was then brought up and balance obtained at a distance, d , from the photometer. Next, the comparison lamp was regulated as above indicated, until the heat balance was obtained, the comparison lamp being at a distance, D , and supplied with power, W , watts. Then, on the assumption that the heat from the comparison lamp was radiated equally in all directions, we have:—

Intensity of radiation at bolometer $\rho = rW/4\pi D^2$ watts per square centimetre, where r is the ratio of radiation to total power.

Intensity of illumination of beam $I = fK/d^2$, where K is the candle-power of the standard lamp, and f the ratio of the illumination in the direction of the beam to the average illumination.

Hence, the mechanical equivalent of light $M = \frac{4\pi\rho}{I} = \frac{Wr}{Kf} \left(\frac{d}{D} \right)^2$, giving the mechanical equivalent in watts per candle.

A careful determination of the candle power of the comparison lamp in various directions, when kept at a constant P.D., was made by Mr. Jolley, resulting, for the horizontal direction, in a reduction factor of 0.862, agreeing very well with the 0.865 given by Paterson.

For the direction in which the radiation was measured the value of the factor was found to be 0.78.

The amount of heat lost by convection was estimated experimentally by measuring the amount of heat communicated to a suitable calorimeter by the warm air rising from the glow lamp. It was found that the convection loss was not more than 2 or 3 per cent., which could be neglected in view of the accuracy which could be obtained.

The greater number of the observations were made in the yellow-green, which were judged by eye to be in the neighbourhood of $\lambda = 0.54 \mu$ proposed by Guillaume. Having regard to the fact that the mounting hardly justified accurate determinations of wave-length; that the point $\lambda = 0.54 \mu$ can hardly be said to have been definitely determined as the point of maximum

efficiency ; that in the region of maximum efficiency the variation would not probably be great, as was confirmed by test ; and lastly, that in order to avoid trouble, owing to the Purkinje effect, it was considered advisable to work at illuminations not exceeding two or three candle-feet, in which case the sensitiveness was not very great, it was considered superfluous to determine the wave-length with greater accuracy. It may be said that the sensitiveness of the arrangement seemed to allow of the definite detection of half a watt at a distance of about 2 metres.

In making determinations on white light, the slit was broadened considerably, and by covering it up from each side successively, it could be adjusted so that light passing one edge of the slit gave a very dark red light on the photometer screen, while that from the other edge gave a deep violet light on it. In this case the result produced by the whole slit was of a pure white light, from which all the invisible radiation was cut off, instead of being only cut off from one end, as in the experiments of Ångström.*

A number of preliminary observations were taken with arc and Nernst lamps as sources of light, and reversing the photometer box, etc. Considerable trouble was, however, found with drifting of the galvanometer, and this was traced to the presence of the observer. The mean result, however, from 24 observations was 0.08 watts per candle power. After this the whole of the apparatus was removed, the photometer bench, sliding screen, etc., being set up in a dark room, through the wall of which an aperture was made for the projection of the spectrum, and a second small aperture for the observation of the photometer. In this way the whole of the observations could be taken without entering the room, and the readings were much more satisfactory.

The results obtained are collected in Table I.

The final result of about 0.12 watt per candle power for the white light from the Nernst filament agrees almost exactly with the value found by Ångström for the Hefner lamps. Thomsen and Tumlriz both used absorption methods, and little value can be attached to their results. Other values can be deduced from investigations on the efficiencies of illuminants, but these values range from 0.0011 to 0.0289 watt per candle found by Wedding, and 0.02 to 0.39 by Rüssner, to 0.19 to 0.49 watt per candle from the results of Merritt.

The lower value of 0.08 watt per candle found in the present tests for

* In Ångström's experiments the glass in the lenses, etc., employed would probably have cut off the major part of the ultra-violet radiation, and the energy in the ultra-violet is generally very small for ordinary sources of light. Hence probably the agreement with our results.

white light from the arc is probably due to the higher temperature of the source. Pending more exact determinations, therefore, it may be assumed that an ideal source of white light should give us about 10 candles per watt, and a monochromatic yellow-green source nearly 17 candles per watt.

Table I.—Observations on the Mechanical Equivalent of Light.

| Standard lamp. | | Comparison lamp. | | | | $M = \frac{W}{0.78 \cdot K} \left(\frac{d}{D} \right)^2.$ |
|-------------------------|------------------------|------------------|----------------------|-----------------|--------------|--|
| Distance, <i>d</i> . | Candle power, K. | Distance, D. | Current, ampères. | P.D., volts. | Watts, W. | |

(A) Light approximately monochromatic, yellow-green.

| | | | | | | |
|----------|------|-------|-------|------|------|--------|
| 80.0 | 24.5 | 116.7 | 0.145 | 31.8 | 4.61 | 0.0555 |
| 80.0 | 24.5 | 106.7 | 0.13 | 29.0 | 3.77 | 0.0455 |
| 70.6 | 24.5 | 165.5 | 0.15 | 32.6 | 4.9 | 0.0468 |
| 78.0 | 20.6 | 165.5 | 0.145 | 31.8 | 4.48 | 0.0620 |
| 78.0 | 20.6 | 165.5 | 0.16 | 34.5 | 5.52 | 0.0765 |
| 78.0 | 24.5 | 165.5 | 0.17 | 36.2 | 6.15 | 0.0715 |
| 85.0 | 24.5 | 165.5 | 0.15 | 32.4 | 4.85 | 0.0670 |
| 76.8 | 24.5 | 165.5 | 0.155 | 33.2 | 5.15 | 0.0573 |
| 7676.3 | 20.6 | 165.5 | 0.145 | 31.6 | 4.58 | 0.0605 |
| 76.8 | 24.5 | 165.5 | 0.15 | 32.2 | 4.83 | 0.0536 |
| 57.4 | 24.5 | 165.5 | 0.23 | 45.0 | 9.9 | 0.0622 |
| 121.0 | 24.5 | 165.5 | 0.095 | 22.2 | 2.11 | 0.0590 |
| Mean ... | | | | | | 0.0598 |

(B) White light from wide slit.

| | | | | | | | |
|----------|------|-------|-------|------|------|--------|----------------------|
| 149.0 | 16.0 | 206.0 | 0.115 | 26.3 | 3.03 | 0.127 | } Nernst filament |
| 86.0 | 13.0 | 263.0 | 0.225 | 47.0 | 16.6 | 0.1115 | |
| Mean ... | | | | | | 0.1193 | |
| 76.1 | 16.0 | 263.5 | 0.23 | 47.5 | 10.9 | 0.073 | } Arc |
| 75.0 | 16.0 | 263.5 | 0.25 | 50.5 | 12.6 | 0.082 | |
| 89.6 | 24.5 | 166.5 | 0.16 | 34.4 | 5.5 | 0.0835 | |
| 89.6 | 24.5 | 166.5 | 0.16 | 34.4 | 5.5 | 0.0835 | |
| Mean ... | | | | | | 0.0805 | |

Table II.—Mechanical Equivalent of Light.
Collected Values.

| Observer. | Date. | Method. | Source. | Unit. | Mechanical equivalent. | | | |
|----------------------------|-------|---------|---------------------------------|---|------------------------|----------|-------------|----------|
| | | | | | Calories per second. | | Watts. | |
| | | | | | Per Hefner. | Per C.P. | Per Hefner. | Per C.P. |
| J. Thomsen | 1863 | A. | Sperm candle | Sperm candle, 8.2 grammes per hour | 0.065 | 0.0733 | 0.276 | 0.3075 |
| " | " | " | Moderator lamp | | 0.0585 | 0.065 | 0.245 | 0.272 |
| " | " | " | Gas flame | | 0.0615 | 0.0683 | 0.257 | 0.286 |
| " | " | " | " | | 0.063 | 0.070 | 0.264 | 0.293 |
| " | " | " | " | " | 0.0553 | 0.0615 | 0.232 | 0.258 |
| O. Tumlirz and Krug | 1888 | A. | Incandescent platinum wire | Hefner..... | 0.041 | 0.0455 | 0.1715 | 0.19 |
| O. Tumlirz | 1889 | A. | Hefner lamp..... | Hefner..... | 0.0455 | 0.0505 | 0.191 | 0.212 |
| K. Ångström ... | 1903 | C. | Hefner lamp..... | Hefner..... | 0.0259 | 0.0288 | 0.1085 | 0.121 |
| Writer and A. C. Jolley | 1907 | C. | Nernst filament | Candle..... | 0.0256 | 0.0284 | 0.107 | 0.119 |
| " | " | " | Arc | " | 0.0173 | 0.0192 | 0.0725 | 0.0805 |
| " | " | " | Monochromatic, yellow- green | " | 0.01285 | 0.0143 | 0.0538 | 0.0598 |

Method A.—Thermopile and absorptive screens.

Method C.—Direct measurement of energy in spectrum.

In this table the Hefner has been taken as 0.90 C.P. See Paterson, 'Proc. Inst. E. E.', vol. 38, p. 286, and Fleming, p. 311.

On the Surface-tension of Liquids investigated by the Method of Jet Vibration.

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(Communicated by Lord Rayleigh, P.R.S. Received June 11,—Read June 27, 1907.)

(Abstract.)

1. According to Lord Rayleigh's theory* of jet-vibrations, measurement of the length of the standing waves and the velocity and cross-section of a jet, together with the density of the liquid, affords the necessary constants for the calculation of the surface-tension.

Notwithstanding the great fundamental advantages of this method, it has only been used in very few cases, and only for relative measurements of the surface-tension.†

The explanation hereof is to be found in the great difficulties connected with the adequate exact determination of the wave-length, and cross-section or velocity of the jet. As none of the methods in use for the measurement of these quantities could be taken as satisfactory, the main object of this investigation has been to work out really good methods for them.

2. The determination of the cross-section of the jet is accomplished in the following manner:—To the lower end of a pendulum is connected an apparatus, the "jet-catcher," consisting of two parallel vessels with rectangular openings, the short sides of which are cutting-edges. The two vessels are parallel to the horizontal jet and symmetrical to each other with regard to a plane through the axis of the pendulum. When this is oscillating the jet-catcher is cutting pieces out of the horizontal jet. From the weight and the length of these pieces "cut out" the cross-section of the jet is calculated.

The different sources of errors are discussed, and it is shown that it is easy to obtain very reliable results by this method. For a water-jet, velocity 278.1 cm. per second, diameter = 0.13415 cm., the mean error in the measured cross-section has been determined to 0.14 per cent.

The velocity of the jet is calculated as the ratio between the discharge and the cross-section.

3. Production of the desired deviation from the cylindrical form of a jet:—

* Lord Rayleigh, 'Roy. Soc. Proc.' vol. 29, p. 71, 1879.

† F. Picard, 'Arch. d. Sc. phys. et nat.' (3), vol. 24, p. 361, 1890; G. Meyer, 'Wied. Ann.' vol. 86, p. 523, 1895.

In the paper is shown the importance of the jet only executing one single vibration, as in other cases the determination of the wave-length is difficult and becomes inaccurate. In the measurements that, up to now, have been made with this method, only little attention has been paid to this condition. I have succeeded in making some orifices so exact, that jets issuing from them practically only execute one vibration.

4. The influence of the amplitude on the period of vibration has been investigated, and it is shown that only for very small amplitudes is the period independent of the amplitude.

5. The determination of the wave-length is very difficult. By all the previous measurements it is determined as the distance between the summits of the jet, and the determination has taken place by direct measurement either on the jet itself or on a photograph of it. As the amplitude of the vibration must be small, this method is very unsatisfactory, and cannot give good results. An exact determination of the wave-length can be made by using the jet itself as an optical, image-forming system. The following method was found to be very convenient:—The jet is illuminated from a parallel, linear, incandescent lamp, and the twice refracted and once reflected rays form an image of the lamp on a photographic plate (compare the theory of the rainbow). If the jet is cylindrical, the image will be a straight line, but for a jet with standing-waves the image will be wave-like. And as the amplitude of the image is much larger than that of the jet, it is much easier to measure the wave-length on the image than on the jet itself.

6. Results.—The surface-tension of the following liquids has been determined:—

| | |
|--|--|
| Water | ($T_{15^{\circ}\text{C.}}$ = 74.30 dyn./cm.). |
| Toluol | ($T_{15^{\circ}\text{C.}}$ = 28.76 „). |
| Aniline | ($T_{15^{\circ}\text{C.}}$ = 43.00 „). |
| 3 aqueous solutions of NH_3 . | |
| 1 „ | solution of CuSO_4 . |
| 1 „ | „ H_2SO_4 . |
| 15 „ | solutions of alcohol. |

For the three first named the results are given above.

7. Used in this manner the jet method gives very consistent results, and is highly deserving of use in the future on account of its great fundamental advantages.

The Dispersion of Double Refraction in Relation to Crystal Structure.

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(Communicated by Professor J. Larmor, Sec. R.S. Received July 5, 1907.)

In a previous communication,* the writer discussed the double refraction of a medium composed of similar particles arranged in rectangular order, the results being applied especially to the effects produced in colloidal solutions by mechanical stress and by a magnetic field; the present paper is the discussion of a similar problem, using a simpler method of procedure suggested by Professor Larmor.† The object is to investigate to what extent it is possible to consider double refraction, whether produced artificially or occurring in natural crystals, as due simply to an æolotropic distribution of similar particles; the questions which arise when one considers whether the æolotropy occurs naturally or is produced by the action of mechanical, electric, or magnetic force are not specially considered, but the various cases are classified in the first section.

In the next sections we consider a medium composed of a homogeneous assemblage of optically isotropic molecules and obtain an expression giving the dispersion of the double refraction. This is applied first to artificial double refraction produced by mechanical stress and by an electric field; then on the same basis the dispersion in quartz is examined. Certain divergences in natural crystals and especially such anomalous cases as apophyllite and vesuvian lead to an extension of the theory. This is, briefly, an æolotropic distribution of optically æolotropic molecules, each of which disperses regularly: it is examined first in relation to uniaxal crystals and finally in general for biaxal crystals, and is found to contain the possibility of all the varieties of dispersion of double refraction which occur in natural crystals.

1. *Theories of Double Refraction.*

The ordinary theory of double refraction, in so far as it is molecular, amounts to considering the medium as a collection of crystal molecules in cubical order, all the varieties of dispersion being postulated of the single particle. Thus with the principal axes as co-ordinate axes, if (f_1, g_1, h_1) be the

* Roy. Soc. Proc. A. vol. 77, p. 170, 1906.

† Loc. cit., p. 180.

polarisation of a typical particle at which the effective electric force is (X_1, Y_1, Z_1) , we have equations of the form

$$\begin{aligned}\frac{\partial^2 f_1}{\partial t^2} + k_1^2 f_1 &= \alpha X_1, \\ \frac{\partial^2 g_1}{\partial t^2} + k_2^2 g_1 &= \alpha Y_1, \\ \frac{\partial^2 h_1}{\partial t^2} + k_3^2 h_1 &= \alpha Z_1.\end{aligned}\tag{1}$$

These equations mean that the æolotropy is assumed to originate wholly in the individual crystal molecule, and that it affects the quasi-elastic force under which the polarisation electrons are supposed to vibrate.

The same method has usually been followed in attempts to apply electron theory to the double refraction due to mechanical stress.

If we consider the equations for an isotropic medium, similar to (1) but with a single constant k , then Voigt* assumes that k is altered by amounts proportional to the stresses in the medium; this is a direct effect on the internal forces of the molecule, while on the other hand a theory which confines the effect to a rearrangement of the molecules in space will express the result by a modification of the effective force (X_1, Y_1, Z_1) in the previous equations.

The latter theory appears to comprise the double refraction effects obtained by Majorana by placing certain colloidal solutions in a magnetic field. These effects appear to be quite distinct from those involved in the Zeemann effect. The double refraction obtained in the latter way is explained by a direct action of the magnetic field on the vibrating electron, and a result of the theory is that the extraordinary and ordinary indices both differ from the index of the isotropic medium under no magnetic action; the variation of the two indices is in the same direction, one being three times the other, and the difference varies inversely as the cube of the wave-length.

In the Majorana effect, on the other hand, the variations of the two indices are in opposite directions, one being approximately twice the other.

The same distinction occurs in the theory of the Kerr effect, that is, of double refraction produced by an electric field. Voigt† has extended his theory of the Zeemann effect to cover an analogous effect by an electric field, the results being of the same character. Now Kerr's experiments appeared to prove that only the index for vibrations parallel to the field was altered; however, in some recent experiments, Aeckerlein‡ claims to have observed in

* Voigt, 'Annalen der Physik,' vol. 6, p. 461, 1901.

† Voigt, 'Annalen der Physik,' vol. 4, p. 197, 1901.

‡ Aeckerlein, 'Physikalische Zeitschrift,' vol. 7, p. 594, 1906; also Voigt, *ibid.*, p. 811, 1906.

certain liquids a change in both indices, the variations being in opposite senses and one apparently twice the other. It is, of course, possible that there may be some direct effect of the electric field upon the periods of the electrons, in addition to a merely mechanical effect of rearrangement of molecules.

For the present we are concerned more with working out the possibilities of the latter supposition; that is to say, although Cauchy's theory of optical dispersion, as caused by simple discreteness of the medium, was insufficient to account for ordinary dispersion, it is suggested that it may be capable of application to the differences of dispersion occurring in different directions in a doubly refracting medium.

2. *Optical Properties of a Homogeneous Assemblage of Isotropic Molecules.*

In a dielectric medium, if we write (X, Y, Z) for the electric force, (α, β, γ) for the magnetic force, and (f, g, h) for the total electric displacement, we have the usual equations

$$\begin{aligned}\text{curl } (\alpha, \beta, \gamma) &= \frac{4\pi}{c} \frac{\partial}{\partial t} (f, g, h), \\ \text{curl } (X, Y, Z) &= -\frac{1}{c} \frac{\partial}{\partial t} (\alpha, \beta, \gamma)\end{aligned}\quad (2)$$

The total displacement (f, g, h) is given by equations of the form

$$\begin{aligned}f &= \frac{1}{4\pi} X + \Sigma f_A, \\ f_A &= N_A f'_A,\end{aligned}\quad (3)$$

where f'_A refers to the polarisation of a typical particle and N_A is the number of such per unit volume.

For f_A we have an equation

$$\frac{\partial^2 f_A}{\partial t^2} + k_A^2 f_A = \alpha_A X_A, \quad (4)$$

where X_A is the component of effective electric intensity considered as acting on the given particle.

The determination of the mean value of X_A is the problem in question, and in particular, the estimation of the influence of neighbouring particles.

In the ordinary procedure, we consider round the given particle a sphere whose radius R is small compared with the wave-length of the radiation crossing the medium, but such that it contains a large number of particles; then we evaluate separately the influence of the particles outside and within this spherical region.

The first part is taken to be the force within a spherical cavity cut in a medium uniformly polarised to the value at the point in question of the vector

$$\left(f - \frac{1}{4\pi} X, \quad g - \frac{1}{4\pi} Y, \quad h - \frac{1}{4\pi} Z\right);$$

this, then, contributes a force

$$\frac{4\pi}{3} (\Sigma f_h, \Sigma g_h, \Sigma h_h).$$

The second part is due to the average effect of the immediately neighbouring particles within the sphere R, and is generally written as

$$4\pi (s_1 \Sigma f_h, s_2 \Sigma g_h, s_3 \Sigma h_h),$$

where s_1, s_2, s_3 are constants depending upon the arrangement of the particles. For a simple cubical arrangement, we take the s -constants to be all zero; thus, as in the similar argument in the case of liquids, we are able to eliminate the consideration of the purely local part of the neighbouring action.

Now, for any other regular arrangement of particles, the s -constants of this method will not all be equal and zero; but suppose that instead of a sphere R, we can choose some other form of surface R', such that we can again ignore the local effect of the particles within R', then we are left with the evaluation of the force within a cavity R' in a medium uniformly polarised to the value of the material polarisation vector at the point in question. In particular, it is clear that for a first approximation for a regular arrangement of particles differing slightly from a simple cubical system, we may assume R' to be an ellipsoid whose axes are nearly equal.

If we take co-ordinate axes in the directions of the principal axes (a, b, c) of the ellipsoid, the force due to the particles outside is now given by

$$A \left(f - \frac{1}{4\pi} X\right), \quad B \left(g - \frac{1}{4\pi} Y\right), \quad C \left(h - \frac{1}{4\pi} Z\right), \quad (5)$$

where
$$A = 2\pi abc \int_0^\infty \frac{du}{(a^2 + u)^{\frac{1}{2}}(b^2 + u)^{\frac{1}{2}}(c^2 + u)^{\frac{1}{2}}} \quad (6)$$

with similar expressions for B and C.

Hence, if we put

$$(a, b, c) = r(1 + \epsilon_1, 1 + \epsilon_2, 1 + \epsilon_3),$$

we have to the first power in $\epsilon_1, \epsilon_2, \epsilon_3$,

$$\begin{aligned} A &= \frac{4\pi}{3} \left\{1 - \frac{4}{3}\epsilon_1 + \frac{2}{3}(\epsilon_2 + \epsilon_3)\right\}, \\ B &= \frac{4\pi}{3} \left\{1 - \frac{4}{3}\epsilon_2 + \frac{2}{3}(\epsilon_3 + \epsilon_1)\right\}, \\ C &= \frac{4\pi}{3} \left\{1 - \frac{4}{3}\epsilon_3 + \frac{2}{3}(\epsilon_1 + \epsilon_2)\right\}. \end{aligned} \quad (7)$$

Writing these for the moment as $4\pi (\frac{1}{3} + s)$, we have, from (4) and (5),

$$\frac{\partial^2 f_h}{\partial t^2} + k_h^2 f_h = \alpha_h \left\{ X + 4\pi (\frac{1}{3} + s) \left(f - \frac{1}{4\pi} X \right) \right\}. \quad (8)$$

If the quantities vary as e^{ikt} , we find from this equation an expression for f_h ; this can be substituted in equation (3) to give a relation between f and X which must necessarily be of the form $f = n^2 X / 4\pi$, where n is the refractive index. Hence we obtain a value for n which is expressed most conveniently in the form

$$\frac{n^2 - 1}{n^2 + 2 + 3s(n^2 - 1)} = \frac{4\pi}{3} \sum_h \frac{\alpha_h}{k_h^2 - k^2} = \frac{n_0^2 - 1}{n_0^2 + 2}, \quad (9)$$

where n_0 is the refractive index of the same substance if isotropic and of the same mean density.

Now we substitute from (7) the values for s and expand from (9) to the first power in the small quantities $\epsilon_1, \epsilon_2, \epsilon_3$; we find the following values for the principal refractive indices of the medium:—

$$\begin{aligned} n_1 &= n_0 - \frac{1}{15} \frac{(n_0^2 - 1)^2}{n_0} \{ 3\epsilon_1 - (\epsilon_1 + \epsilon_2 + \epsilon_3) \}, \\ n_2 &= n_0 - \frac{1}{15} \frac{(n_0^2 - 1)^2}{n_0} \{ 3\epsilon_2 - (\epsilon_1 + \epsilon_2 + \epsilon_3) \}, \\ n_3 &= n_0 - \frac{1}{15} \frac{(n_0^2 - 1)^2}{n_0} \{ 3\epsilon_3 - (\epsilon_1 + \epsilon_2 + \epsilon_3) \}. \end{aligned} \quad (10)$$

The mean value n_0 is given by

$$n_0 = \frac{1}{3} (n_1 + n_2 + n_3). \quad (11)$$

The medium, then, is doubly refracting, and we shall consider first some consequences when it behaves like a uniaxial crystal.

In this case we may take ϵ_2 and ϵ_3 as zero, and we have the extraordinary index n_1 and the ordinary index n_2 given by—

$$\begin{aligned} n_1 &= n_0 - \frac{2}{15} \frac{(n_0^2 - 1)^2}{n_0} \epsilon, \\ n_2 &= n_0 + \frac{1}{15} \frac{(n_0^2 - 1)^2}{n_0} \epsilon, \end{aligned} \quad (12)$$

where

$$n_0 = \frac{1}{3} (n_1 + 2n_2).$$

The mean index, that is the index for the same medium if isotropic and of the same density, lies unsymmetrically between the ordinary and extraordinary indices, being twice as far from the latter as from the former. Further, if we measure the double refraction δ by the difference between the two principal indices, we have

$$\delta = n_2 - n_1 = \frac{1}{5} \frac{(n_0^2 - 1)^2}{n_0} \epsilon. \quad (13)$$

Assuming, then, that the ellipticity of the effective ellipsoid is constant, if we know how n_0 varies with the wave-length, this equation gives a law of dispersion of the double refraction; we shall compare this law with some experimental data in the following sections.

3. *Double Refraction Due to Mechanical Stress.*

The most suitable test for the above formula would be in the case of artificially produced double refraction, as, for instance, when an isotropic medium behaves like a uniaxial crystal if subjected to mechanical stress. However, in these cases the effect is extremely small, and the principal indices n_1 and n_2 have not usually been measured separately, but simply their difference. If the dispersion of the unstrained isotropic medium were known either by a curve or a dispersion formula, then it would be possible to calculate the dispersion of the difference $n_1 - n_2$; for instance, if n_0 , for the isotropic medium of the same density, were given by

$$n_0 = a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4},$$

then, since

$$\delta = n_1 - n_2 = \frac{(n_0^2 - 1)^2}{n_0} C,$$

we should have δ given approximately by a relation of the form

$$\delta = p + \frac{q}{\lambda^2} + \frac{r}{\lambda^4}. \quad (14)$$

Further, the separations of n_1 and n_2 from n_0 should be in opposite directions, with the former approximately twice the latter. These consequences rest on the initial assumption of the theory, namely, that the isotropic medium is, in fact, an assemblage of optically isotropic molecules, and not a collection of crystalline molecules, with their axes distributed equally in all possible directions.

4. *Electric Double Refraction.*

For the double refraction produced in media by the action of an electric field, Kerr observed a dispersive effect, and supposed that the double refraction varied inversely as the square root of the wave-length, but this has been shown to be erroneous by Blackwell.* His experiments deal with carbon disulphide, and curves are given for the variation of the double refraction with the wave-length for two different temperatures with a field strength of 56,000 volts per centimetre. These results give the only data suitable for the present purpose.

* H. L. Blackwell, 'American Academy Proceedings,' vol. 41, p. 647, 1906.

We have, then, two sets of values for the double refraction δ of CS_2 at the temperatures of 11°C. and 24°C. , each set giving values for six different wave-lengths with the value of δ for $\lambda = 589$ and $t = 24^\circ$ taken as 100; absolute values can be obtained by means of a determination of 7.04×10^{-7} for δ at the latter point.

For the present theory we require the actual values of n_1 and n_2 in order to calculate the mean value n_0 , equal to $(n_1 + 2n_2)/3$; however, it is sufficient to take for n_0 the refractive index of CS_2 under the same conditions in regard to density and temperature.

To obtain these values for the wave-lengths required, we have a dispersion formula for CS_2 at 18° obtained by Martens,* which gives values correct to four decimal places at least; the formula is

$$n^2 = m + \frac{m'\lambda^2}{\lambda^2 - \lambda'^2} - k\lambda^2,$$

where $m = 1.63403$; $k = 0.000300$;
 $m' = 0.88113$; $\lambda' = 217.53$.

The correction for temperature can be made to sufficient accuracy by allowing a decrease of index of 9×10^{-4} for each degree rise of temperature.† Making these calculations, we have the values of n_0 used in the following Tables I and II. The first column gives the wave-length λ , the second n_0 , the third the observed values of the double refraction δ ; the fourth column gives the calculated values of $\delta n_0 / (n_0^2 - 1)^2$, which, according to the theory, ought to be constant.

Table I.—Carbon Disulphide at 24° .

| λ . | n_0 . | $\delta_{\text{obs.}} = n_1 - n_2$. | $C = \delta n_0 / (n_0^2 - 1)^2$. | $\delta_{\text{calc.}}$. |
|-------------|---------|--------------------------------------|------------------------------------|---------------------------|
| 421.6 | 1.678 | 119.4 | 60.78 | 118.8 |
| 441.5 | 1.668 | 115.0 | 60.39 | 115.2 |
| 467.7 | 1.656 | 110.5 | 60.27 | 110.9 |
| 508.5 | 1.642 | 106.0 | 60.50 | 106.0 |
| 538.7 | 1.634 | 103.0 | 60.35 | 103.2 |
| 589.0 | 1.624 | 100.0 | 60.58 | 99.8 |

Mean value of $C = 60.48$; greatest divergence = 0.5 per cent. approx.

The fifth column in each table was obtained by using the mean value of C , together with the values of n_0 , in order to recalculate the values of δ . A comparison of the third and fifth columns shows the amount of agreement between the observed and calculated values of δ ; it may be remarked that

* Martens, 'Annalen der Physik,' vol. 6, p. 632, 1901.

† Landolt, 'Tabellen,' 3rd edition, p. 671.

the observed values are the mean values of results varying by as much as 2 per cent.

Table II.—Carbon Disulphide at 11°.

| λ . | n_0 . | $\delta_{\text{obs.}} = n_1 - n_2$. | $C = \delta n_0 / (n_0^2 - 1)^2$. | $\delta_{\text{calc.}}$ |
|-------------|---------|--------------------------------------|------------------------------------|-------------------------|
| 421·6 | 1·689 | 125·6 | 61·80 | 125·7 |
| 441·5 | 1·679 | 121·0 | 61·40 | 121·8 |
| 467·7 | 1·667 | 116·8 | 61·62 | 117·2 |
| 508·5 | 1·653 | 112·4 | 62·01 | 112·1 |
| 538·7 | 1·645 | 109·4 | 61·93 | 109·2 |
| 589·0 | 1·635 | 106·6 | 62·26 | 105·9 |

Mean value of $C = 61·84$; greatest divergence = 0·7 per cent. approx.

We can calculate the absolute value of C from the value for δ at $t = 24^\circ$ and $\lambda = 589$, viz., $7·04 \times 10^{-7}$. If, then, ϵ is the ellipticity of the effective ellipsoidal cavity of the theory, we have ϵ equal to $5C$, and we find the following values:—

$$\begin{aligned}\epsilon &= 0·000,002,18 \text{ at } 11^\circ, \\ \epsilon &= 0·000,002,13 \text{ at } 24^\circ.\end{aligned}\tag{15}$$

5. Dispersion of Double Refraction in Quartz.

In order to determine to what extent the double refraction of natural crystals can be accounted for by an æolotropic distribution of isotropic molecules, we require data for some simple crystal for which the difference of the indices is sufficiently small; for this purpose we have accurate determinations of n_1 and n_2 for quartz extending over a very wide range of wave-lengths. The values for these given in Table III are by Martens* for wave-lengths ranging from 185 to 768, and by Carvallo† from 801 to 1849.

The numbers in the fifth column C are calculated in each case from the relations

$$C = \frac{\delta n_0}{(n_0^2 - 1)^2}; \quad n_0 = \frac{1}{2}(n_1 + 2n_2).$$

Then the quantity C ought to be a constant. Remembering that we have neglected terms of the second order, and omitting for the present the extreme limits in the ultra-violet and infra-red, we see that the figures give considerable support to the theory. For throughout the large range of λ , from 358 to 1159, C does not differ from a mean value of 0·007245 by as much as 0·2 per cent. in any case. For the sake of comparison one might

* Martens, 'Annalen der Physik,' vol. 6, p. 628, 1901.

† Carvallo, 'Comptes Rendus,' vol. 126, p. 730, 1898.

calculate the values of some other relation which might suggest itself; for instance, the quantity $\delta n_0/(n_0^2-1)$ decreases continuously throughout the whole range, its extreme values differing from a mean value by as much as 16 per cent.

Table III.—Quartz.

| λ . | n_1 . | n_2 . | δ . | $C \times 10^6$. |
|-------------|---------|---------|------------|-------------------|
| 185 | 1.68988 | 1.67571 | 0.01417 | 7151 |
| 198 | 6394 | 5087 | 1307 | 7150 |
| 224 | 3231 | 2045 | 1186 | 7175 |
| 242 | 1647 | 0522 | 1125 | 7170 |
| 263 | 0386 | 1.59306 | 1080 | 7174 |
| 281 | 1.59518 | 8467 | 1049 | 7188 |
| 308 | 8564 | 7547 | 1017 | 7204 |
| 340 | 7787 | 6747 | 0.00990 | 7223 |
| 358 | 7369 | 6390 | 979 | 7236 |
| 394 | 6805 | 1.55846 | 959 | 7235 |
| 434 | 6389 | 396 | 943 | 7235 |
| 467 | 6034 | 102 | 932 | 7231 |
| 486 | 1.55897 | 1.54967 | 930 | 7253 |
| 508 | 746 | 822 | 924 | 7246 |
| 533 | 599 | 680 | 919 | 7246 |
| 546 | 534 | 617 | 917 | 7245 |
| 560 | 461 | 546 | 915 | 7251 |
| 589 | 335 | 424 | 911 | 7252 |
| 627 | 186 | 280 | 906 | 7253 |
| 643 | 131 | 227 | 904 | 7253 |
| 656 | 091 | 189 | 902 | 7247 |
| 670 | 047 | 145 | 902 | 7258 |
| 768 | 1.54794 | 1.53903 | 891 | 7238 |
| 801 | 725 | 834 | 891 | 7257 |
| 832 | 661 | 773 | 888 | 7250 |
| 867 | 598 | 712 | 886 | 7250 |
| 905 | 532 | 649 | 883 | 7245 |
| 946 | 464 | 583 | 881 | 7245 |
| 991 | 392 | 514 | 878 | 7240 |
| 1042 | 317 | 442 | 875 | 7246 |
| 1097 | 238 | 366 | 872 | 7232 |
| 1159 | 152 | 283 | 869 | 7232 |
| 1229 | 057 | 192 | 865 | 7224 |
| 1307 | 1.53951 | 090 | 861 | 7218 |
| 1396 | 832 | 1.52977 | 855 | 7202 |
| 1497 | 692 | 842 | 850 | 7198 |
| 1615 | 524 | 679 | 845 | 7201 |
| 1749 | 319 | 485 | 834 | 7164 |
| 1849 | 163 | 335 | 828 | 7154 |

In consequence of the use of Babinet's compensator in determining the double refraction of minerals, the dispersion of double refraction in quartz has been studied extensively. From experimental observations in the visible and ultra-violet spectrum, Macé de Lépinay* found that δ could be represented very accurately by a formula—

$$\delta = a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4}.$$

* Macé de Lépinay, 'Annales de la Faculté des Sciences de Marseille,' vol. 50, p. 1, 1891.

The numerical values of the constants were found by Carvalho to fit also his observations in the infra-red. This relation is of the form to be expected from our formula connecting δ and n_0 , assuming n_0 to be expressible by a dispersion formula of the usual type.

We have assumed in the calculations that the effective cavity was an ellipsoid of small ellipticity. We might then examine the order of magnitude of the second order terms which have been neglected, but it is simpler to obtain now a more general relation free from this approximation.

Using the notation of equations (5) to (9), the only assumption we make about the effective cavity is that the force within it, due to the polarised medium outside, has components

$$\begin{aligned} 4\pi \left(\frac{1}{3} + s_1\right) \left(f - \frac{1}{4\pi} X\right), \\ 4\pi \left(\frac{1}{3} + s_2\right) \left(g - \frac{1}{4\pi} Y\right), \\ 4\pi \left(\frac{1}{3} + s_3\right) \left(h - \frac{1}{4\pi} Z\right), \end{aligned} \quad (16)$$

where s_1, s_2, s_3 are constants.

Then assuming as before that the molecules are isotropic, we have a principal index given by

$$\frac{n^2 - 1}{n^2 + 2 + 3s(n^2 - 1)} = \frac{n_0^2 - 1}{n_0^2 + 2}.$$

The quantity $(n^2 + 2)/(n^2 - 1)$ differs by a constant from its value in any other state; or, more simply, we have

$$\frac{1}{n^2 - 1} = \frac{1}{n_0^2 - 1} - s. \quad (17)$$

Consequently, if the medium is uniaxal, we have the relation

$$\frac{1}{n_2^2 - 1} - \frac{1}{n_1^2 - 1} = \text{constant}, \quad (18)$$

where n_1 and n_2 are the extraordinary and ordinary indices.

Using the values given in Table III, we can examine this relation for quartz; the result is shown in Table IV.

Table IV.—Quartz.

| λ . | C' . | C' . | λ . |
|-------------|---------|---------|-------------|
| 358 | 0·01439 | 0·01443 | 656 |
| 434 | 0·01439 | 0·01439 | 768 |
| 486 | 0·01442 | 0·01442 | 832 |
| 583 | 0·01441 | 0·01442 | 905 |
| 580 | 0·01442 | 0·01440 | 991 |
| 627 | 0·01442 | 0·01439 | 1097 |

$$C' = (n_2^2 - 1)^{-1} - (n_1^2 - 1)^{-1}. \quad \text{Mean value} = 0·01441.$$

6. *Some Exceptional Crystals.*

The relation obtained in (18) does not cover all the cases of regular dispersion, as we see from the figures for Iceland Spar given in Table V. But it may be noticed that in this case the double refraction δ is 20 times greater than in quartz; thus simple distribution of isotropic molecules is apparently not quite sufficient to account for so large a difference between the two indices.

Table V.—Iceland Spar.

| λ . | $\delta = n_2 - n_1$. | $C' = (n_1^2 - 1)^{-1} - (n_2^2 - 1)^{-1}$. |
|-------------|------------------------|--|
| 410 | 0·1837 | 0·2581 |
| 434 | 0·1812 | 0·2578 |
| 508 | 0·1757 | 0·2565 |
| 589 | 0·1719 | 0·2555 |
| 656 | 0·1698 | 0·2548 |
| 768 | 0·1671 | 0·2538 |

Further, we have exceptional cases in which δ decreases with the wave-length, but much more rapidly than in other crystals. For instance, in strontium hyposulphate, the rate of decrease is about 10 times that of quartz, and we find that the quantity C of the previous calculations is by no means constant, but decreases with the wave-length.

If we have δ , given by the relation

$$\delta = \frac{1}{2} \frac{(n_0^2 - 1)^2}{n_0} \epsilon,$$

we see that the substance may be either a positive or negative uniaxal crystal, according as ϵ is negative or positive; but in either case the absolute value of δ decreases with n_0 , that is, in general, δ will decrease as λ increases. Now this is the rule in most actual crystals, but there are a few for which δ increases with λ , although n_0 diminishes; the figures for apophyllite are given in Table VI for the purpose of comparison with a later set of figures.

Table VI.—Apophyllite.*

| λ . | δ . |
|-------------|------------|
| 486·1 | 0·00218 |
| 501·6 | 0·00232 |
| 546·1 | 0·00241 |
| 587·6 | 0·00265 |
| 589·6 | 0·00265 |
| 656·3 | 0·00284 |
| 667·8 | 0·00289 |

* B. Trolle, 'Physikalische Zeitschrift,' vol. 7, p. 700, 1906.

Also, there are crystals for which δ passes through a minimum, and some for which the double refraction changes from positive to negative—the substance being isotropic for some definite wave-length.

It appears, then, that a theory of æolotropic distribution of isotropic molecules which may serve for the artificial double refraction produced in isotropic bodies and for simple crystals is not sufficient to cover the varieties of dispersion found in natural crystals. This is naturally to be expected; for, in addition to the varieties of dispersion in biaxial crystals, to be considered later, we see that if such a simple theory were sufficient, then the symmetry of all the physical properties of a crystal would be the same as its optical symmetry, and this is not the case. The direction in which to modify the theory is clear; we shall consider a crystalline medium as a homogeneous assemblage of crystal molecules. Whether or no the crystal molecule can be identified with the chemical molecule need not be considered here. Leaving the general theory till later, we shall consider first the case of a uniaxial crystalline medium.

7. *Modified Theory of Uniaxial Crystals.*

The previous theory can be extended in the following manner:—The molecules (or crystal units) of the medium are not necessarily to be supposed ellipsoidal in shape, but are optically æolotropic, so that the subsidiary equations connecting the polarisation of a particle with the effective electric force are æolotropic, with an axis of symmetry; the particles are supposed to be arranged in a homogeneous assemblage such that the effective cavity may be taken as an ellipsoid of revolution of ellipticity ϵ , and having its axis of symmetry coincident in direction with that of the crystal unit. Then, instead of equation (9), we have now

$$\frac{n_1^2 - 1}{n_1^2 + 2 + 3s_1(n_1^2 - 1)} = \frac{4\pi}{3} \sum_k \frac{\alpha_k}{k_k'^2 - k^2} = \frac{n_{01}^2 - 1}{n_{01}^2 + 2}, \quad (19)$$

with a similar equation in n_2 and n_{02} .

In these, n_{01} and n_{02} are the extraordinary and ordinary indices for the substance, with a regular cubical arrangement of the same molecules in the same density.

Hence, substituting for s_1 and s_2 their values in terms of ϵ , we have the two principal indices given by

$$\begin{aligned} n_1 &= n_{01} - \frac{2}{15} \frac{(n_{01}^2 - 1)^2}{n_{01}} \epsilon, \\ n_2 &= n_{02} + \frac{1}{15} \frac{(n_{02}^2 - 1)^2}{n_{02}} \epsilon, \end{aligned} \quad (20)$$

And the double refraction δ is given by

$$\delta = n_{01} - n_{02} - \frac{1}{15} \left\{ \frac{2(n_{01}^2 - 1)^2}{n_{01}} + \frac{(n_{02}^2 - 1)^2}{n_{02}} \right\} \epsilon. \quad (21)$$

These equations (20) and (21) would represent the effect of deformation in a natural uniaxial crystal. For the present purpose we apply them to a natural unstrained crystal. They cannot be verified by actual calculation in this case, but we shall see that they cover all the anomalous cases mentioned in the previous section.

To find how δ varies with the wave-length, we have, from (21),

$$\frac{\partial \delta}{\partial \lambda} = \left\{ 1 - \frac{2}{15} \frac{(3n_{01}^2 + 1)(n_{01}^2 - 1)}{n_{01}^2} \epsilon \right\} \frac{\partial n_{01}}{\partial \lambda} - \left\{ 1 - \frac{1}{15} \frac{(3n_{02}^2 + 1)(n_{02}^2 - 1)}{n_{02}^2} \epsilon \right\} \frac{\partial n_{02}}{\partial \lambda}. \quad (22)$$

Now the object is to account for anomalous dispersion of δ in regions free from absorption. Then if n_{01} and n_{02} follow the regular law of diminishing as λ increases, we have both $\partial n_{01}/\partial \lambda$ and $\partial n_{02}/\partial \lambda$ negative; and as we can have n_{01} greater or less than n_{02} and ϵ positive or negative, we see that it is possible to have $\partial \delta/\partial \lambda$ positive. In fact, it is possible to have the following varieties of change of δ as λ increases: (i) slow decrease, (ii) rapid decrease, (iii) slow increase, (iv) δ passing through a minimum, and (v) δ changing in sign.

These cases all occur, being typified by quartz, strontium hyposulphate, apophyllite, and for the latter cases by varieties of vesuvian and melilite.*

The theory can be illustrated best by building up from a known crystal of regular dispersion of double refraction one which behaves like apophyllite. Suppose we consider the uniaxial crystal phenakite, for which there are available determinations of the principal indices for five different wave-lengths; we denote these indices by n_{01} and n_{02} , and we find that their difference diminishes as the wave-length increases. Suppose, now, that the crystal molecules of phenakite are rearranged so that the effective cavity has an ellipticity of 0.035, and has its axis along the direction of the axis of symmetry of the crystal units; then by equation (21) we may calculate the double refraction δ of the medium thus built up. The results are shown in Table VII. We see that although the double refraction of the phenakite crystals follows the regular law of decreasing as λ increases, yet the resulting double refraction δ of the distorted medium increases as λ increases, and is of about the same order as that of apophyllite (Table VI). This is, of course, only intended as an illustration of the possibility of explaining the irregular dispersion in regions which are not in the vicinity of absorption bands.

* Hlawatsch, 'Tschermak's Mitteilungen,' vol. 23, p. 415, 1904.

Table VII.—Phenakite with $\epsilon = 0.035$.

| λ . | n_{01} . | n_{02} . | $n_{01} - n_{02}$. | δ . |
|-------------|------------|------------|---------------------|------------|
| 508 | 1.67451 | 1.65858 | 0.01593 | 0.00255 |
| 537 | 1.67254 | 1.65664 | 0.01590 | 0.00260 |
| 589 | 1.66977 | 1.65394 | 0.01583 | 0.00265 |
| 643 | 1.66735 | 1.65154 | 0.01581 | 0.00273 |
| 670 | 1.66639 | 1.65060 | 0.01579 | 0.00275 |

8. *Dispersion in Biaxial Crystals.*

We consider now the previous theory in the most general form, namely, the double refraction of a medium composed of optically æolotropic particles with the same orientation and arranged so as to give an ellipsoidal effective cavity with its principal axes in any three fixed mutually perpendicular directions; we shall indicate briefly the general character of the results.

We take the principal axes of a typical particle as co-ordinate axes, and have $(\lambda_1, \mu_1, \nu_1)$, $(\lambda_2, \mu_2, \nu_2)$, and $(\lambda_3, \mu_3, \nu_3)$, as the direction cosines of the principal axes of the effective cavity. Then if (f', g', h') is the polarisation of the medium, the x -component of the force within the cavity due to the polarisation is given by

$$X_1 = (\lambda_1^2 A + \lambda_2^2 B + \lambda_3^2 C) f' + (\lambda_1 \mu_1 A + \lambda_2 \mu_2 B + \lambda_3 \mu_3 C) g' + (\lambda_1 \nu_1 A + \lambda_2 \nu_2 B + \lambda_3 \nu_3 C) h', \quad (23)$$

where A, B, C , are the usual constants for the cavity and can be written as—

$$(A, B, C) = \frac{4\pi}{3} + 4\pi (s_1, s_2, s_3).$$

Further, if we write n_{01}, n_{02}, n_{03} for the principal indices of a medium composed of the same units, but arranged in regular cubical order, we have three equations of the form

$$\frac{n_{01}^2 - 1}{n_{01}^2 + 2} = \frac{4\pi}{3} \sum_k \frac{\alpha_k}{k_{1k}^2 - k^2}. \quad (24)$$

We can obtain now three equations connecting the components of electric force (X, Y, Z) with the polarisation (f', g', h') ; but if (l', m', n') are the direction cosines of a principal axis of the resulting ellipsoid of polarisation and if n is the corresponding principal index of refraction for this direction, we must have

$$l' f' + m' g' + n' h' = \frac{n^2 - 1}{4\pi} (l' X + m' Y + n' Z). \quad (25)$$

Hence, for the determination of the principal axes and indices of the medium we obtain three equations of the type

$$\left(a_{11} - \frac{1}{n_{01}^2 - 1} + \frac{1}{n^2 - 1} \right) l' + a_{12} m' + a_{13} n' = 0, \quad (26)$$

where the a -constants are given by relations of the form

$$a_{11} = \lambda_1^2 s_1 + \lambda_2^2 s_2 + \lambda_3^2 s_3; \quad a_{23} = \mu_1 \nu_1 s_1 + \mu_2 \nu_2 s_2 + \mu_3 \nu_3 s_3. \quad (27)$$

We shall examine now the various types of crystals covered by these equations.

(a) *Prismatic system*.—If we take the simplest case, we have the principal axes of the crystal unit coinciding with those of the effective cavity; then evidently the three principal polarisation axes are in the same directions, and maintain these directions for all wave-lengths, as in crystals of the prismatic type.

From equations (26) and (27) we see that the principal refractive indices are given by

$$\frac{1}{n_r^2 - 1} - \frac{1}{n_{0r}^2 - 1} + s_r = 0; \quad r = 1, 2, 3. \quad (28)$$

Thus we have

$$n_r = n_{0r} + \frac{1}{2} \frac{(n_{0r}^2 - 1)^2}{n_{0r}} s_r. \quad (29)$$

Hence, as in the theory of § 7 for uniaxal crystals, we may have the indices varying differently, with the wave-length and consequently the possibility of such crystals as brookite, in which the order of magnitude of the indices changes and the plane of the optic axes is turned through a right angle.

(b) *Monoclinic System*.—Suppose, now, that one principal axis of a particle coincides with a principal axis of the cavity, then this will be an axis of the polarisation ellipsoid which is fixed in direction; thus we obtain the monoclinic system of crystals with a single plane of symmetry. Without discussing the equations in detail, we consider, as an illustration, the dispersion of the other two polarisation axes. These are at right angles to each other and lie in the plane of symmetry of the crystal. Let ϕ be the angle giving their position with reference to the fixed co-ordinate axes, and α the corresponding angle for the position of the fixed axes of the effective cavity in the same plane.

Then, supposing the plane of symmetry to be the (2, 3) plane, we find, after substitution in (26) and (27) and reduction, that

$$\tan 2\phi = \frac{(s_2 - s_3) \sin 2\alpha}{(s_2 - s_3) \cos 2\alpha - (n_{02}^2 - 1)^{-1} + (n_{03}^2 - 1)^{-1}}. \quad (30)$$

Now s_2 , s_3 , and α are assumed to be independent of the wave-length; suppose, then, that the indices n_{02} and n_{03} for the crystal molecules in cubical order decrease regularly with the wave-length, so that on the simplest supposition we have dispersion formulæ of the type

$$n_{0r}^2 = a + \frac{b}{\lambda^2}.$$

Then from (30) we see that the dispersion of the angle ϕ is given by a relation of the form

$$\tan 2\phi = \frac{p + q\lambda^2 + r\lambda^4}{p' + q'\lambda^2 + r'\lambda^4}. \quad (31)$$

Sufficient experimental data on the dispersion of the principal axes of monoclinic crystals are not available to test this formula; but a similar relation without terms in λ^4 has been suggested on other grounds by Nakamura,* and found to agree fairly well with some cases.

(c) *Anorthic System*.—Finally we have the general case in which none of the axes of the crystal unit coincides with a principal axis of the effective cavity, and consequently the three principal axes of polarisation all change, both in magnitude and direction, with the wave-length; this includes, then, all anorthic crystals.

9. Summary.

Beginning with a theory intended to apply to artificial double refraction produced in an isotropic medium, we found that the consequences could be expressed simply in the following manner:—If n is a refractive index of the substance, the quantity $(n^2 - 1)^{-1}$ is altered by an amount independent of the wave-length, and varying only with the direction; this implies a small change in n which is proportional to $(n_0^2 - 1)/n_0$, where n_0 refers to a standard state of arrangement in regular cubical order.

Passing to natural crystals, we find anomalous dispersion of the double refraction occurring in regions away from absorption bands, and a theory modified to account for these cases leads to a consideration of the optical relations of crystal structure. In this connection it is of interest to compare some recent work in two directions. On the one hand we have attempts to explain crystal structure as a function of chemical constitution; the crystal is described as a homogeneous assemblage of spheres which are combined into sub-groups defining the crystal unit or molecule. On the other hand, we have work connecting the dispersion of double refraction in certain groups of minerals with their chemical constitution, some members being found to possess a minimum of double refraction.†

Consequently, it should be possible to explain the varieties of dispersion of double refraction by means of the structure of the crystal, and we have attempted this in the previous sections, with the following assumptions:—The crystal unit contains vibrating electrons, so that their combined effect is expressed by three principal equations connecting the polarisation of the

* Nakamura, 'Physikalische Zeitschrift,' vol. 6, p. 172, 1905.

† Hlawatsch, *loc. cit.*

44 *Dispersion of Double Refraction in Relation to Crystal Structure.*

unit with the effective electric field ; if, then, these units are arranged in regular cubical order, we have a medium with principal refractive indices along three fixed directions in space, and we assume that in this case we have regular decrease of the double refraction with increasing wavelength in regions away from absorption bands. But considering in general any other homogeneous assemblage, we express the effect by a change in the effective electric field acting on the crystal unit; this effect we have estimated by supposing, as a sufficient approximation, that the effective cavity is slightly ellipsoidal instead of being spherical. Thus differences of packing of the crystal molecules are represented optically by variations in the ratios of the axes of the effective cavity and in their directions in space compared with the polarisation axes of the individual unit. Combining these assumptions, we have shown that they are sufficient for a descriptive theory covering the varieties of dispersion of double refraction found in natural crystals.

Experiments on a New Cathode Dark Space in Helium and Hydrogen.

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[PLATE 1.]

In a paper recently read before this Society,* the author described some experiments on the length of the Crookes dark space under varying conditions in different gases. While the gas hydrogen was under this investigation, a slight inequality of light was noticed very close to the cathode, which, under the prevailing conditions, was not definite enough to warrant further attention at the time. When, however, helium was introduced into the apparatus, this phenomenon became strikingly clear, showing itself to be a hitherto undescribed dark space very close against the cathode and inside the Crookes dark space, possessing very different properties from the latter. By the time the measurements of the Crookes dark space in helium were completed, the behaviour of the new dark space had suggested a simple explanation, which led to a series of experiments, of which this paper is a description.

Apparatus.—The preliminary observations of the new dark space were made in the “guard ring cathode” discharge tube already described,† but when it was realised that an accurate knowledge of the current density was not required, this was replaced by a smaller cylindrical tube, 8 cm. in diameter, with more uniform walls and plane aluminium cathode and anode. With this exception, the apparatus was entirely as described in the previous paper.

Measurement of the Length of the New Dark Space.—As this is exceedingly small (its greatest length under measurable conditions is about 0.1 cm.), its measurement was found to be a matter of considerable difficulty; any attempt at magnification by a telescope was, as with the Crookes dark space, worse than useless, and, after trying several methods of micrometry, the plain sighter used for the latter was adopted as being the most reliable. This consisted of a tube about 20 cm. long, fitted at one end with a pointer and at the other with a small eye-hole, the whole being mounted to move parallel to the edge of the cathode. The readings were done in darkness, the error being about ± 0.002 cm.

* F. W. Aston, “Experiments on the Length of the Cathode Dark Space,” ‘Roy. Soc. Proc.,’ A, vol 79, 1907, pp. 80—95.

† *Loc. cit.*

Theory of the New Dark Space.—The preliminary measurements of “ d ,” the length of the new dark space, showed that it was practically independent of the pressure and roughly proportional to the inverse square root of the current density. Now the equation expressing the distribution of electric force X in the Crookes dark space was shown in the previous paper* to hold under certain assumptions,

$$X = (8\pi cx/\lambda)t,$$

where c = current density, x = distance from the edge of the Crookes dark space, and λ = velocity of a $+$ ion in a unit field at prevailing pressure. If we substitute D (the length of the Crookes dark space) for x in this expression, we obtain the field just outside the cathode and, since D is roughly proportional to λ , this field is independent of the pressure and proportional to $c^{1/2}$, indicating that the fall of potential across d is constant.

Now suppose the electrons start from the surface of the cathode from rest or with a uniform velocity not great enough to ionise the gas. It is clear that, if the energy necessary for such ionisation is constant, they can only attain this energy by falling through a definite potential, so that there will be a space in front of the cathode of definite length in which no ionisation will go on at all, and where no light would be expected. The new dark space may therefore be regarded as *the distance through which the electrons fall in order to attain sufficient energy to ionise the gas by collision with its molecules.*

The influence of the current density upon this phenomenon explains the fact of its being overlooked during the work on the Crookes dark space in hydrogen, since only high-current densities were then employed.

The first test of the above theory is the constancy of the fall of potential. This, by the distribution of force quoted, is $\frac{3}{2}Vd/D(1 - \frac{1}{2}(d/D)^2) + \dots$ where V is the total fall of potential across the Crookes dark space, which in the absence of any trace of positive column, has been shown to be practically the same as the difference of potential between the electrode surfaces. Since d is very much smaller than D , and the error of its measurement is comparatively great, the second term may be neglected. The following tables for hydrogen and helium show that, over a large range, the fall of potential across the new dark space is constant within experimental error and is for *hydrogen* 15 volts, *helium* 30 volts.

Assuming for the value of the charge on an electron 3.4×10^{-10} C.G.S., it gives for the *minimum energy required to ionise an atom of hydrogen* 1.7×10^{-11} ergs; *of helium*, 3.4×10^{-11} ergs. Again, taking 1.7×10^7 as the value of e/m in electromagnetic units, the *minimum ionisation velocity is for hydrogen*, 2.25×10^8 cm. per second; *helium*, 3.2×10^8 cm. per second.

* *Loc. cit.*

† *Loc. cit.*

Appearances of the New Dark Space.—Fig. 1 gives a diagrammatic section of the cathode discharge in helium at about 1 mm. pressure, with a comparatively low current density. The appearance may be broadly divided

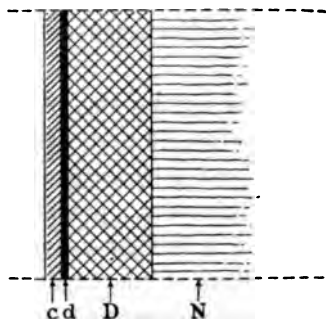


FIG. 1.

c, cathode ; *d*, new dark space ; *D*, Crookes dark space ; *N*, negative glow.

into three bands: an intensely black one of the order of 0.05 cm., the new dark space, followed by a region of moderate greenish light of length about 1 cm., the Crookes dark space, terminating finally in the brilliant bluish-green "negative glow."

Plate 1, fig. 1, is an actual photograph of the discharge, clearly showing the relative proportions. As the camera was placed close to and level with the cathode, the curvature of the edge of the Crookes dark space is greatly exaggerated.

Plate 1, fig. 2, shows the appearance of the discharge at a very much lower current density. The Crookes dark space has lost all its distinctness of outline, while the new dark space is still sharply defined, and much larger than in fig. 1.

The theory given above is well supported by the intense blackness of the new dark space in pure helium and hydrogen, and by this theory the following effect was predicted:—

Consider the motion of the first generation of electrons starting from rest at the surface of the cathode in a field, for simplicity assumed uniform. Let d be the distance through which they must freely fall in such a field to obtain sufficient velocity to ionise the gas. If d is smaller than the mean free path of an electron under such conditions, we should expect just beyond d a maximum ionisation and a corresponding maximum light, gradually fading as we recede from the cathode and the energy of the electrons is dissipated. But, by the time a point $2d$ from the cathode is reached, the second generation of electrons, formed by collisions at d , will have attained

ionisation velocity, so that there should be another, but less sharply defined maximum of light at a point just beyond $2d$, another beyond $3d$, and so on each getting more indistinct, so that the faint light in the Crookes dark space should be striated near the cathode. It is clear that this effect will be at its maximum when d is of the same dimensions as the mean free path of an electron under stated conditions.

Of this effect only the first maximum was observed in hydrogen, but in helium, at comparatively high pressures and very low current densities, the striation could be plainly seen and photographed. Fig. 3, Plate 1, is the reproduction of the discharge in helium at a pressure (beyond the range of the manometer) of 2 to 3 mm. With a current so small as barely to cover the surface of the cathode, the curvature of the edge of the new dark space, due to the current density not being uniformly distributed over the cathode, is clearly shown. Three distinct maxima, and traces of a fourth, could be detected on the original negative. It is interesting to note that the potential between the electrodes in this particular experiment was well below 200 volts so that the effect can be shown with ease by means of a suitable tube and an ordinary lamp circuit.

In such striated discharges the distances between the cathode and the first maximum and between the first and second maxima, after allowance is made for the distribution of electric force, correspond to equal falls of potential as nearly as can be estimated. This conclusion is of importance for, since the second maximum is caused presumably by electrons formed from molecules of the gas itself, their initial velocity must be negligible; therefore the initial velocity of those causing the first maximum must similarly be negligible, so that in helium the electrons may be taken as starting from an aluminium cathode at rest, and the values of minimum ionisation, energy, and velocity already evaluated for that gas become approximately absolute.

Occurrence of the New Dark Space.—It was naturally expected that this interesting phenomenon—for which the name “primary cathode dark space” has been suitably suggested—might be detected in other gases when the best conditions for its exhibition had been discovered. Up to the time of writing, however, not the slightest indication of it has been observed in air, nitrogen, oxygen, argon, or carbon monoxide. For this two explanations are naturally suggested if the theory given above is substantially correct, either—

- (i) The molecules of these gases have so low an ionisation energy that “ d ” is too small to be detected;
- (ii) The electrons liberated from the surface of aluminium by the impact



FIG. 1.



FIG. 2.



FIG. 3.

The white line on the left of each of the figures represents the position of the edge of the cathode.

of positive ions of these gases start with sufficient velocity to ionise at their very outset, in which case the phenomenon would not exist at all.

Some results obtained from observation of the length of d in mixtures of helium and oxygen, which require further investigation, show that the latter is the more probable explanation.

In conclusion, I wish to express my heartiest thanks to Professor J. H. Poynting for his kind help and encouragement throughout this research.

Table I.—Hydrogen.

Table II.—Helium.

| V. | D. | d . | dV/D . | V. | D. | d . | dV/D . |
|-------|-------|-------|----------|-------|-------|-------|----------|
| 345 | 0·625 | 0·018 | 10·0 | 204 | 0·381 | 0·039 | 20·9 |
| { 225 | 1·220 | 0·058 | 10·7 | { 202 | 0·496 | 0·051 | 20·8 |
| { 314 | 0·975 | 0·030 | 9·7 | { 275 | 0·407 | 0·032 | 21·4 |
| { 273 | 2·355 | 0·090 | 10·4 | { 200 | 0·610 | 0·061 | 20·0 |
| { 295 | 1·890 | 0·070 | 10·9 | { 271 | 0·562 | 0·048 | 20·3 |
| { 443 | 1·540 | 0·035 | 10·0 | { 200 | 0·887 | 0·087 | 19·6 |
| { 276 | 2·660 | 0·088 | 9·3 | { 275 | 0·780 | 0·059 | 20·1 |
| { 361 | 2·250 | 0·067 | 10·8 | { 325 | 1·010 | 0·064 | 20·5 |
| { 517 | 2·020 | 0·042 | 10·7 | { 420 | 1·472 | 0·072 | 20·4 |
| { 318 | 3·040 | 0·086 | 9·0 | { 590 | 1·422 | 0·047 | 19·5 |
| { 405 | 2·620 | 0·066 | 10·2 | { 550 | 1·932 | 0·067 | 19·1 |
| { 510 | 2·425 | 0·047 | 9·9 | { 730 | 1·762 | 0·048 | 19·5 |
| { 415 | 3·850 | 0·093 | 10·0 | { 454 | 2·710 | 0·121 | 20·3 |
| { 545 | 3·410 | 0·067 | 10·6 | { 530 | 2·499 | 0·098 | 20·7 |
| { 840 | 2·920 | 0·037 | 10·6 | { 770 | 3·168 | 0·090 | 21·8 |

V = Potential difference in volts between electrodes.

D = Length of Crookes dark space in cm.

d = Length of new dark space in cm.

The pressures range in hydrogen from 0·1 to 1·0 mm., in helium from 0·4 to 3·0 mm. The measurements were performed at the same pressure.

On the Presence of Sulphur in some of the Hotter Stars.

By Sir NORMAN LOCKYER, K.C.B., LL.D., Sc.D., F.R.S.

(Received May 8,—Read June 20, 1907.)

[PLATE 2.]

In connection with a particular study of the green region of stellar spectra, photographs of the spectra of several of the brighter stars have recently been obtained at Kensington, using the two 6-inch Henry prism. An excellent photograph of the spectrum of Rigel is amongst those secured, and the increased dispersion available has afforded evidence which abundantly verified my previous conclusions as to the presence of sulphur in the hotter stars. With regard to the occurrence of sulphur, I stated in 'Inorganic Evolution,' p. 169, "The evidence also suggests sulphur, and this is all the more probable because of the simplicity of its spectrum series."

In the course of the reduction to wave-lengths of the lines in this recent Rigel photograph, an isolated clearly defined line was found at about λ 4815, which had not been observed in any previously studied stellar spectra. Reference to Watts' 'Index of Spectra' showed that there was a strong line of sulphur close to that position recorded by Hasselberg. On referring to Eder and Valenta's record* of the sulphur spectrum, a strong line was found of wave-length 4811·967. This was so large a discrepancy from Hasselberg's wave-length that a Kensington photograph of the spark spectrum of sulphur was examined, and a very strong and isolated sulphur line was found at λ 4815·3 as nearly as could be estimated. It thus became fairly obvious that the wave-length 4811·967 given by Eder and Valenta was, for some reason or other, in error. Dr. Eder was communicated with in reference to this line with the result that he explained the discrepancy as being due to a clerical error in publishing the wave-lengths. It should have been 4814·967.

To test further whether there was a real identity between the stellar and the laboratory lines, the new Rigel spectrum was carefully examined in the region covered by the characteristic group of sulphur lines extending from λ 4142 to λ 4175. It was found that there were stellar lines—none of them very strong, but undoubtedly genuine—agreeing, as nearly as could be estimated, with each of the members of that group. Other parts of the spectrum also showed lines in the position of other strong sulphur lines. In fact, there are only about three of the strongest sulphur lines, in the region

* 'Beiträge zur Photochemie und Spectralanalyse,' p. 282, Vienna, 1904.

where a comparison is possible, which appear to be lacking in the stellar spectrum. These exceptions will be discussed later.

The following table gives the wave-lengths of the strongest sulphur lines as measured from the Kensington photographs of the vacuum-tube and spark spectra, the vacuum-tube wave-lengths of the corresponding lines as recorded by Eder and Valenta, and the wave-lengths and intensities of the Rigel lines which closely agree in position with the sulphur lines. For the sulphur lines beyond λ 4553, Eder and Valenta's wave-lengths of the vacuum-tube lines are used in the tables, as the existing Kensington photographs of the sulphur spectrum in that region are not of sufficient dispersion to furnish accurate reductions to wave-length. In the region 4100—4553 the Kensington reductions of the wave-lengths of the sulphur lines are given in the table for both vacuum-tube and spark spectra. The former were reduced by means of Hartmann's formula from a photograph taken with the 3-inch Cooke spectrograph, the latter by a direct comparison of the Rowland grating spectra of the sulphur spark and the sun.

The wave-lengths of the stellar lines were obtained in most cases by interpolation between lines whose wave-lengths are well known. For several of the fainter lines which would not stand magnification under the micrometer the wave-lengths were obtained as accurately as possible by direct comparison with a solar spectrum photographed with the same instrument.

The stellar wave-lengths must be accepted as only provisional, but they are probably accurate within 0.3 tenth-metres.

A comparison of the wave-lengths of the sulphur lines, as reduced from the spark spectrum and vacuum-tube spectrum respectively, shows that in nearly all cases the vacuum-tube wave-lengths are about 0.5 tenth-metres less than the spark wave-lengths. This has been pointed out before by Eder and Valenta,* who give a photographic comparison of some of the stronger sulphur lines as they respectively occur in the vacuum-tube spectrum and the spark spectrum, and show that the sharply defined lines of the former occupy positions near the more refrangible edges of the diffuse lines of the latter. Notable exceptions to this, as was also pointed out by Eder and Valenta, are the two strong lines at $\lambda\lambda$ 4253.8, 4285.1 which show practically no shift in passing from one spectrum to the other. These two lines occur quite prominently in all the Kensington spectra of sulphur, under whatever conditions they have been obtained, but they are of a different nature to the other strong sulphur lines, being far more compact and sharply defined. In Hagenbach and Konen's record of the sulphur spectrum, the reproductions of their photographs show these lines as having far inferior intensity to those

* 'Beiträge zur Photochemie und Spectralanalyse,' Plate 15, Vienna, 1904.

Comparison Table of the Strongest Lines of Sulphur and Lines in Rigel.

| Kensington sulphur lines. | | | | Eder and Valenta. | | Rigel (Kensington). | | Remarks. |
|---------------------------|---------------|---------|---------------|-------------------|---------------|---------------------|---------------|---|
| Vacuum tube. | | Spark. | | Vacuum tube. | | | | |
| λ. | Int. Max. 10. | λ. | Int. Max. 10. | λ. | Int. Max. 10. | λ. | Int. Max. 10. | |
| 4142·46 | 5 | 4143·00 | 5 | 4142·39 | 8 | 4142·8 | 1 | Forms with pFe 4178·6 a broad hazy line in Rigel. Apparently lacking in star. These two lines of sulphur are, however, different in nature from the others, being much more sharply defined. Eder and Valenta show also that they behave differently from other S lines |
| 4145·25 | 6 | 4145·75 | 6 | 4145·27 | 7 | 4145·5 | 1 | |
| 4153·81 | 9 | 4153·85 | 9 | 4153·27 | 9 | 4153·7 | 1-2 | |
| 4162·81 | 10 | 4163·80 | 10 | 4163·86 | 10 | 4163·0 | 2-3 | |
| 4174·46 | 5-6 | 4174·95 | 7 | 4174·47 | 7 | p 4174·6 | p 2 | |
| 4253·63 | 10 | 4253·70 | 10 | 4253·77 | 10 | } | — | |
| 4285·03 | 8 | 4285·10 | 7 | 4285·13 | 8 | | | |
| 4294·61 | 5-6 | 4295·20 | 7 | 4294·56 | 8 | 4294·3 | 1 | |
| 4464·67 | 4 | 4464·90 | 6 | 4464·63 | 5 | 4464·5 | 1 | |
| 4524·95 | 6-7 | 4525·20 | 7 | 4525·16 | 6 | 4525·3 | 1-2 | |
| 4552·53 | 4 | — | — | 4552·59 | 5 | 4552·8 | 2 | |
| | | | | 4716·88 | 4 | 4715·9 | 1-2 | |
| | | | | 4814·97 | 4 | 4815·7 | 3 | |
| | | | | 4917·41 | 4 | 4917·6 | 1 | |
| | | | | 4924·27 | 5 | 4924·1 | 4 | |
| | | | | 4925·49 | 6 | 4925·7 | 1 | |
| | | | | 4992·15 | 5 | 4992·5 | 1 | |
| | | | | 5009·76 | 6 | 5010·0 | 1-2 | |
| | | | | 5014·25 | 8 | 5014·4 | 1 | |
| | | | | 5037·41 | 4 | 5027·8 | 1-2 | |
| | | | | 5032·66 | 8 | 5032·9 | 3 | |

* Probably masked by strong Pt line. Stellar line partly due to Si 4552·8

Stellar line chiefly due to pFe 4924·11

NOTE.—The wave-lengths of the spark lines in the region less refrangible than λ 4552·59 are, in general, about 0·5 tenth-metres higher than the corresponding lines of the vacuum-tube spectrum, as given by Eder and Valenta.

of the same lines in the Kensington and Eder and Valenta's photographs. It seems fairly probable, then, that under certain conditions these sulphur lines disappear from the laboratory spectra, and that similar conditions pertain in the absorbing atmosphere of the star, in the spectrum of which the lines in question cannot be traced.

Another line which is doubtfully present in the star is that at λ 4295. There are several weak lines in Rigel from about 4290 to 4303, most of them probably due to proto-iron or proto-titanium, but the nearest to the wavelength of the sulphur line appears to be about 4294.3.

With the possible exception of line 4163.0, none of the Rigel lines given in the preceding list is given by Pickering* in his record of lines in the stellar spectrum. He gives a line at 4163.9 and makes it identical with 4163.9 in α Cygni. Comparison of the Kensington two-prism photographs of these two stellar spectra, however, shows most distinctly that they are not identical. The Rigel line is probably 4163.0 (sulphur), that in α Cygni undoubtedly 4163.9 (proto-titanium).

The following table contains the lines recorded by Keeler† in the spectrum of Rigel in the region between H_β and D. He did not give any origins for the majority of the lines. The probable origins added to the table are suggested as a result of the Kensington investigations of the relation of the stellar lines to lines in terrestrial spectra.

| Rigel lines (Keeler). | | Probable origin (Kensington). | λ of probable origin. |
|-----------------------|--------------------------|--|-------------------------------|
| λ . | Remarks. | | |
| 4861 | H_β . Very strong. | { Asterium Proto-iron Asterium Proto-iron Sulphur Silicon (Group II) Proto-iron Proto-iron Sulphur | 4922.10 |
| 4924 | Fairly strong | | 4924.11 |
| 5016 | Strong | | 5015.73 |
| 5088 | Very weak | | 5018.63 |
| 5066 | Weak | | 5088.0 |
| 5168 | Fe? Fairly strong | | 5067.0 |
| 5316 | Weak | | 5169.22 |
| 5454 | Weak | | 5316.79 |
| 5876 | D_β . Very strong. | | 5454.0 |
| 5890? | D_2 } Suspected. | | |
| 5896? | D_1 } | | |

It will be seen that the only lines not traceable to elements which have— from considerations of lines in other parts of the stellar spectrum—been

* 'Annals Harv. Coll. Obs.,' vol. 28, Part I, p. 79.

† 'Ast. and Ast. Phys.,' vol. 13, p. 489.

found to be represented in the star are the two lines 5033 and 5454. As there are, according to Eder and Valenta, two strong sulphur lines at $\lambda\lambda$ 5032.66 and 5454.00 respectively, it would appear that this is genuine confirmatory evidence that sulphur is really represented in the Rigel spectrum. The line 5033 is well marked in the Kensington stellar spectrum, but Keeler's line 5454 is beyond the region over which the Kensington photograph extends. There are several other strongly marked sulphur lines in the region 5400 to 5500, and it is quite probable that if stellar photographs are obtained extending more into the yellow than the existing one, these lines will also be found to occur in the stellar spectrum.

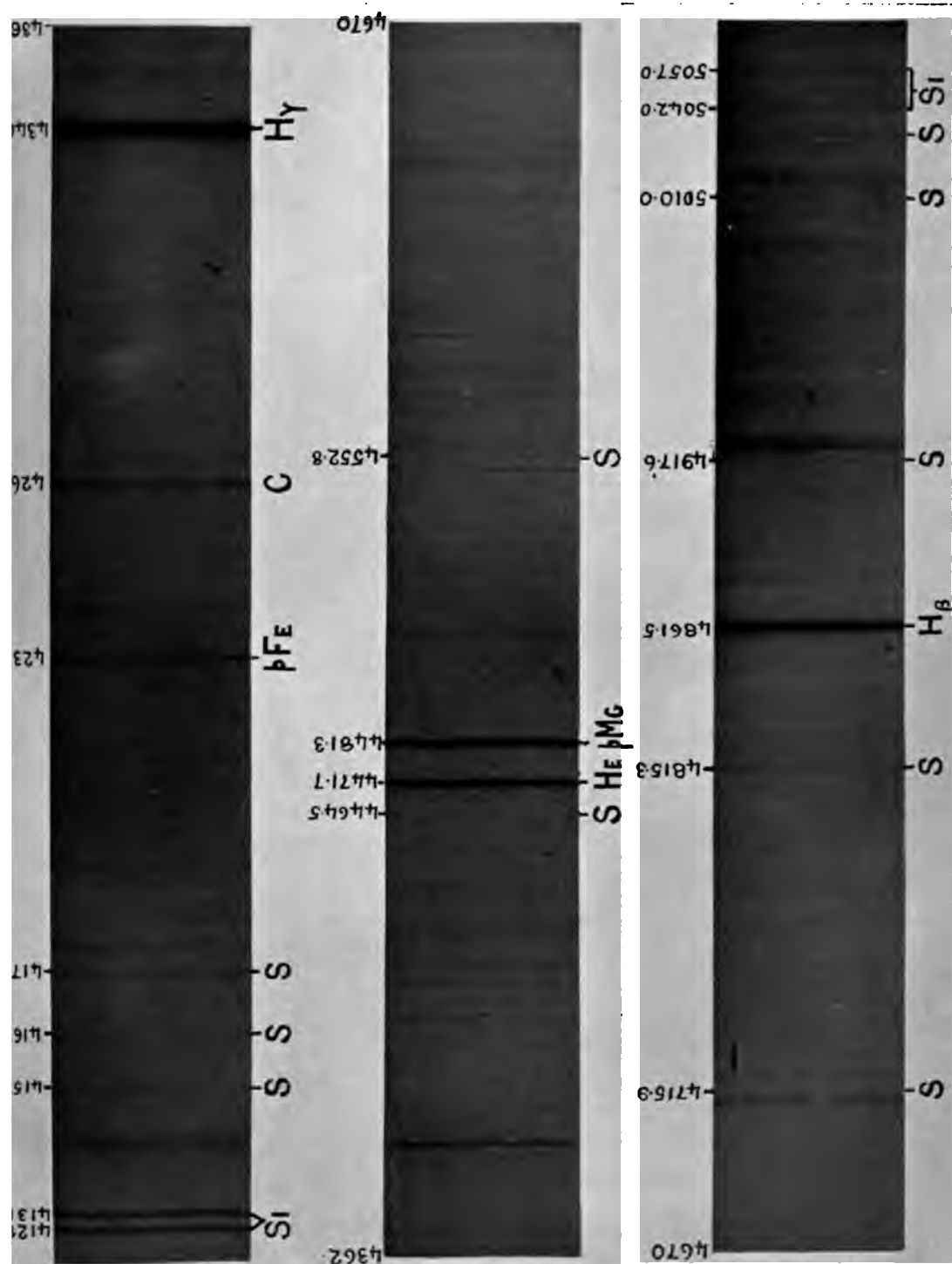
The best-marked Rigel lines which are probably due to sulphur have been looked for in the spectra of α Cygni and Sirius, which represent the next lower stage on the temperature classification. The lines cannot, however, be traced. If they do really exist in these spectra, they are so exceedingly faint as to defy detection in the existing stellar photographs. In Bellatrix, however, representing a higher stage than Rigel, some of the stronger Rigel-sulphur lines, of which may be mentioned 4715.9 and 4815.7, are certainly present, but not so well marked as in Rigel. A really successful photograph of the Bellatrix spectrum has not, however, been yet obtained with the two prisms, and it is expected that when one is obtained other sulphur lines will be traced. It has not yet been possible to investigate whether the lines occur at the Alnitamian stage, as no satisfactory spectrum of a star of this type has yet been photographed with two prisms.

The excellent photograph of the Rigel spectrum in which the sulphur lines were traced was obtained by Mr. W. E. Rolston. The stellar lines were found, and their identity with the sulphur lines established, by Mr. F. E. Baxandall, who, with the assistance of Mr. H. E. Goodson, reduced the wave-lengths of the stellar and terrestrial lines. The photographs of the sulphur spectrum used in the discussion were taken by Mr. C. P. Butler. Mr. Baxandall has also taken part in the preparation of the paper.

REFERENCE TO PLATE.

PLATE 2 shows the spectrum of Rigel, from λ 4123 to λ 5075. The stronger sulphur lines which occur in the spark are denoted by S. The origins and wave-lengths of several of the outstanding lines of the stellar spectrum are also indicated.

An up-and-down positive was first obtained from the original negative, a direct negative then made from it, and from this a seven-times-enlarged positive print. The scale of the reproduction is about six times that of the original negative.



[*Addendum, October 17, 1907.*]

Since the foregoing paper was written, further facts have been obtained regarding the occurrence of sulphur lines in the hotter stars. In the paper it was mentioned that two strong sulphur lines of special behaviour, 4253·8, 4285·1, are lacking in the Rigel spectrum, in which the strongest ordinary spark lines occur. These two lines have since been found to exist in spectra representing higher stages of temperature than that of Rigel, such as γ Orionis (Crucian) and ϵ and κ Orionis (Alnitamian). Reference to Pickering's* records of stellar spectra shows that he also gives the lines in the stars named below, thus:—

| Star (Pickering). | Type (Kensington). | λ . | Int. |
|--------------------|--------------------|--------------------|--------|
| β Centauri | Crucian | { 4254·1 4285·1 | 4 3 |
| ϵ Orionis | Alnitamian | { 4254·1 4285·1 | 3 2 |
| γ Orionis | Crucian | { 4254·1 4285·1 | 2 2 |
| α Pavonis | Crucian | { 4254·1 4285·1 | 1 0 |

It will be noticed that the relative intensity of the two lines is, in general, the same in the different stars, 4254·1 being the stronger. This agrees with their relative intensity in the sulphur spectrum itself.

In a paper on "The Spectra of Silicon, Fluorine, and Oxygen," Lunt† records an oxygen line at 4254·22, and associates it with a stellar line at the same wave-length. In the light of the other oxygen lines occurring in the Crucian and Alnitamian stars, the stellar line in question is too strong to be accounted for solely by the oxygen line, which is relatively weak. The true origin is far more likely to be sulphur, especially as the line is generally accompanied by 4285·1, which cannot be attributed to oxygen. In fact, the two stellar lines under discussion cannot be satisfactorily explained by reference to the lines of any of the other elements already shown to be represented in Crucian and Alnitamian stars. These are helium, hydrogen, silicon, calcium, magnesium, oxygen, nitrogen, and carbon.

As these sharply-defined lines in the sulphur spectrum decrease in intensity, relatively to the diffuse lines, when self-induction is introduced, we should expect them to appear at a higher level of stellar temperature than the set of sulphur lines which appears in Rigel (in which star, it must be remembered, the sharp lines are missing). The fact, therefore, that there are

* 'Annals Harv. Coll. Obs.,' vol. 28, Part II, p. 236.

† 'Annals of the Cape Observatory,' vol. 10, p. 33 B.

56 *Note on the Association of Helium and Thorium in Minerals.*

corresponding lines in the Crucian and Alnitamian stars, which come higher up the temperature curve than the Rigelian, seems to leave no doubt as to the genuineness of the identification.

The Rigelian group of sulphur lines has not been detected in ϵ Orionis, though one or two of the strongest lines have been traced in the best Kensington spectrum of Bellatrix (Crucian). The following represents the relative and inverse behaviour of the two sets of lines in stellar spectra.

| Group. | Type star. | Sharp lines (4254, 4285). | Diffuse lines. |
|------------|--------------------|--|---|
| Alnitamian | ϵ Orionis | Well shown | Absent |
| Crucian | γ Orionis | Present, but weaker than in ϵ Orionis | Strongest lines present, but weaker than in β Orionis |
| Rigelian | β Orionis | Absent | Well shown |

Note on the Association of Helium and Thorium in Minerals.

By the Hon. R. J. STRUTT, F.R.S.

(Received September 10,—Read November 7, 1907.)

The question has been often raised of whether or not helium is a product of thorium radio-activity. My own view throughout has been that it is.* Mr. Boltwood has recently argued that the helium in radio-active minerals may always be attributed to the action of the uranium-radium series of transformations.† I wish in the present note to draw attention to a case where that view is clearly untenable.

Prof. Julius Thomsen, of Copenhagen, described, in 1898,‡ a helium mineral from Ivitgut, Greenland, similar in some respects to fluor spar, but containing rare earths. Recently he has determined the quantity of helium liberated on heating as 27 c.c. per kilogramme.§

Prof. Thomsen kindly sent me a supply of this mineral. I have carefully tested it for radium, and find that it contains no more than the traces which are ubiquitous in rocks and minerals. The quantity found was, in fact, about

* 'Roy. Soc. Proc.,' vol. 73, p. 191, 1904, also March 2, 1905.

† 'Am. J. Sci.,' vol. 23, February, 1907, p. 77.

‡ 'Zeita. Physikalische Chemie,' vol. 25, part 3.

§ 'Bull. de l'Acad. Royale des Sciences, Copenhagen,' 1904, 53—57.

the same as in average rocks, and is insufficient to account for one-hundredth part of the helium present.

On the other hand, a solution of the mineral gave abundant thorium emanation. I am inclined to think that there is some unknown complication about the thorium-emanating power of solutions, which makes it unsafe, in certain cases at least, to infer from it the quantity of thorium present. But enough thorium emanation was given off by the solution to show that thorium was a substantial constituent of the mineral. I regard it as entirely certain that the helium in this mineral has not been generated *in situ* by uranium or radium, and have no hesitation in connecting it with the presence of thorium.

On the Measurement of Temperatures in the Cylinder of a Gas Engine.

by Professor H. L. CALLENDAR, F.R.S., and Professor W. E. DALBY, M.A.,
M.Inst.C.E.

(Received October 8,—Read November 7, 1907.)

1. *Introductory.*—It is important in the experimental investigation of the internal combustion engine to be able to measure directly the temperature of the working fluid at some point of the cycle. If the temperature at a suitable point of the cycle is known, the laws of gases enable us to calculate the temperature at any other point during compression and expansion from the indicator diagram on the assumption that the mass remains constant and that the molecular change occurring in combustion is known. The method usually employed has been to estimate the temperature at the beginning of compression (the temperature at this point is sometimes referred to as the suction temperature") by computing the total mass of the cylinder contents at this point from a knowledge of the gas and air supply and an estimate of the temperature and mass of the contents of the clearance space. But this is an indirect and troublesome method, and some of the data required are extremely uncertain. Direct measurements of the temperature in the cylinder under working conditions have hitherto failed for various reasons. Professor F. W. Burstall* was the first to employ the platinum thermometer for this purpose. He used wires 0·0025 and 0·0015 inch in diameter, and obtained a good deal of valuable information from his experiments, but he

* 'Phil. Mag.,' June, 1895.

did not succeed in measuring the temperature under ordinary working conditions. In his latest report* he says:—

“All attempts to use these wires with an engine firing at every second revolution resulted in the destruction of the wire before a sufficient number of observations could be taken. The temperatures have, therefore, been measured on an engine running dead light, that is firing about one in six of the possible explosions.”

These conditions are quite abnormal, and the results from these experiments cannot, therefore, throw much light on the question of the temperatures corresponding to full load conditions.†

Professor B. Hopkinson‡ has recently suggested that the suction temperature might be measured with a wire sufficiently thick to withstand the explosion temperature without melting, and has developed an ingenious method of correcting the indications of a thick wire so as to deduce the temperature of the gas in the cylinder. The method of correction, though somewhat elaborate, appears to have been satisfactory for temperatures up to 300° C., but his final conclusion is as follows:—

“The large size of the wire (namely, 0·004 inch) was chosen because it was intended ultimately to use it for measuring the suction temperature when the engine was working in the ordinary way, taking in and firing a charge of gas. But it was found that even this large wire always fused before any observations could be taken. A still thicker wire might of course have been used for the purpose, but the correction would then have been so great as to make the results valueless.”

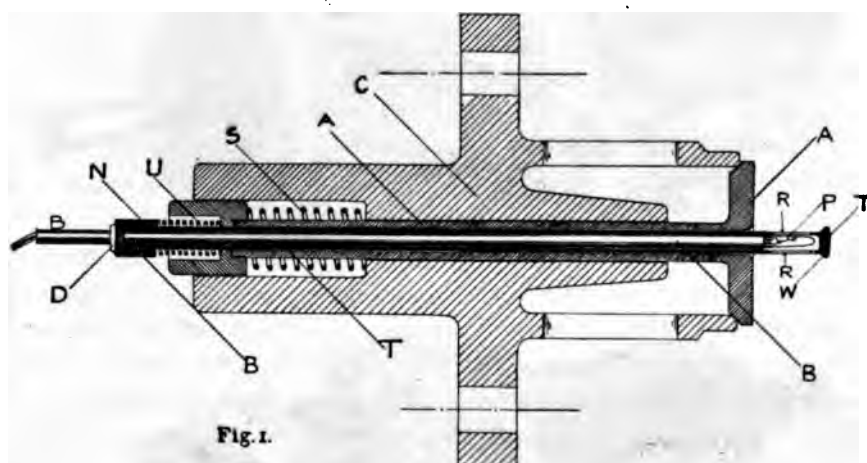
2. *Method employed by the Authors.*—In order to avoid troublesome and uncertain corrections, it is necessary that the wire employed should be fine enough to follow the changes of temperature of the gas very closely during suction and compression. To employ such a wire in the cylinder under working conditions, it is further necessary that it should be perfectly screened from the flame during explosion. Any apparatus for the introduction and withdrawal of the thermometer must be such as not to make any change in the usual form and extent of the clearance surface during the time interval comprising the end of compression. Otherwise the normal conditions of working would be changed, and a risk of pre-ignition would be introduced. The arrangement used by the authors was designed to satisfy these conditions. The thermometer was contained in a small valve (T, fig. 1), called the

* ‘Proc. Inst. Mech. Eng.’ October, 1901, p. 1030.

† The mixtures used were very weak, being one of gas to 12 of air, and the correction for radiation error at the maximum temperatures is very large.

‡ ‘Phil. Mag.’ January, 1907.

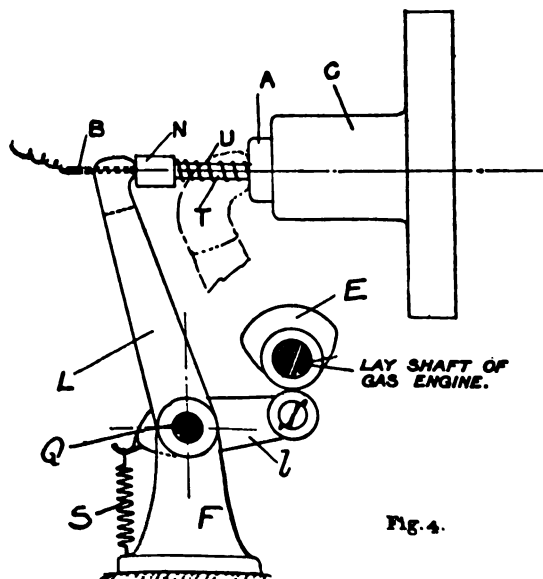
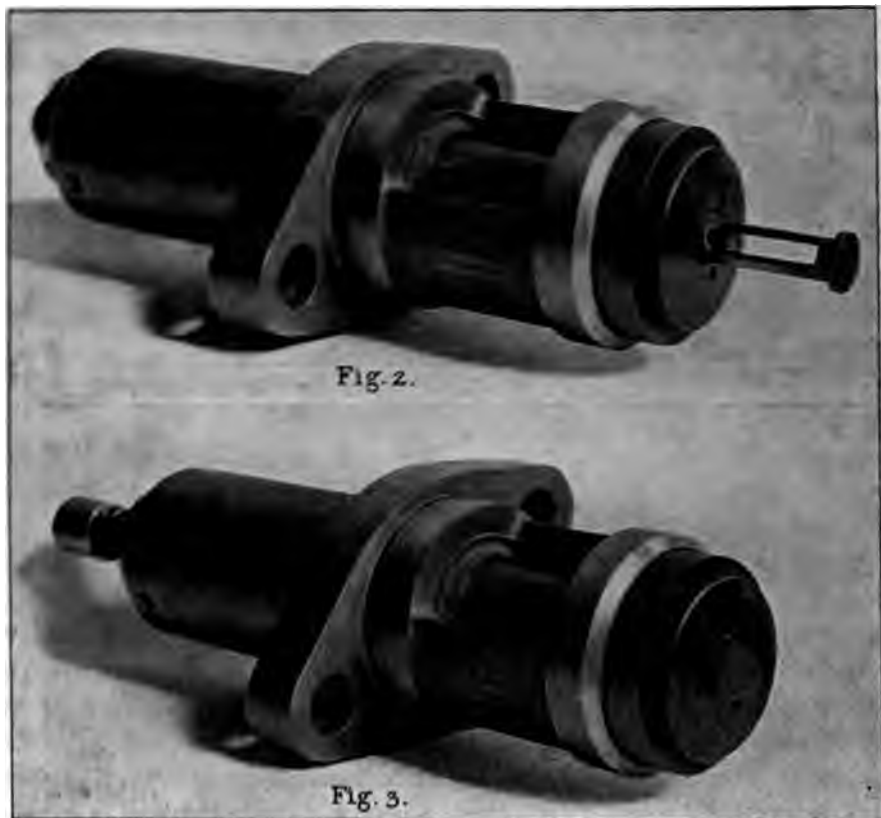
thermometer valve, inserted through the spindle of the admission valve A, which was bored out to receive it. The admission valve casting C is shown detached from the engine cylinder, and the thermometer valve T is shown



open to its fullest extent, the maximum lift being 1.5 inches. The head W of the valve T has a seating in the head of the admission valve A. The valve T is closed by a spring U, shown in compression, acting on a nut N. The thermometer leads are enclosed in a brass tube B fitting inside the spindle of the valve T. The tube can be inserted or withdrawn without dismounting the valve. It is held in place by a collar D which is screwed home against the nut N. The platinum wires forming the thermometer are seen at P. The head W of the valve T is connected to the tube forming the spindle by the two ribs R and R, which are made as thin as possible in order to leave the platinum wires freely exposed to the gas when the valve is pushed in.

Two views of the combined admission and thermometer valves are shown in figs. 2 and 3 reproduced from photographs, fig. 2 showing the thermometer valve opened to its fullest extent, fig. 3 showing it closed.

The gear for operating the thermometer valve is shown diagrammatically in fig. 4. A fixed casting F carries a shaft Q, to which is keyed a long lever L, and a short lever l. The short lever ends in a roller which is held up by a spring against the cam E, keyed to the lay shaft of the engine. The end of the long lever L acts on the nut N at the end of the thermometer valve T, and is forked so as to clear the brass tube B of the thermometer. The end of the lever operating the admission valve A is similarly forked to clear the thermometer valve T. Any desired timing of the exposure of the thermometer valve T in the cylinder may be obtained by adjusting the form



and position of the cam E. In the gas trials described below the thermometer valve was arranged to open during suction and close towards the end of compression.

3. *The Platinum Thermometers.*—The platinum thermometers and accessory apparatus for observing the temperatures were similar to those employed by Callendar and Nicholson in their experiments on the steam-engine,* but the thermometers were of somewhat simpler construction, since they were not required to be exposed to high pressures or temperatures. The leads were a pair of twin wires, insulated with rubber and cotton, and were fixed gas tight in the brass containing tube. The projecting ends of the copper leads were held in place with mica washers. A loop of platinum wire, 0.001 inch diameter and 1 inch long, was soldered to the ends of the thermometer leads. The ends of the compensator leads were similarly connected by a loop of the same wire, $\frac{1}{4}$ inch long. The thermometer and compensator were connected to opposite sides of the Wheatstone bridge, so that the bridge reading gave the difference of resistance between them, corresponding to the resistance of the middle $\frac{1}{4}$ inch of the thermometer loop. This provision of a compensating loop has often been overlooked, but is most essential when using short loops of fine wire for the measurement of rapidly varying temperatures. The ends of the fine wire loops close to the leads are affected by conduction of heat to or from the leads, and cannot follow the rapid variations of temperature; but the end effect is eliminated by observing the difference between two loops of different lengths. The lengths of the loops were chosen so as to give with the wire actually employed a change of resistance of 1 ohm approximately for 100° C. Shorter lengths might have been employed without material reduction of sensitiveness, but the above lengths were found to be sufficiently stiff to stand the commotion in the cylinder satisfactorily for long periods. After each run the thermometer was removed and placed in a tube in a vessel of water. Its resistance was then measured at the temperature of the laboratory, in order to test for variations of the zero. It was found that the zero was generally raised after a run of half an hour or so by about one-fifth of a degree C., owing to slight strain or distortion of the wire; but it was easy to take account of these small changes, which would not, if neglected, however, have materially affected the accuracy of the measurements. The current employed in measuring the resistance was about the 1/200 part of an ampere. The heating effect of this current on the thermometer was measured and found to be less than a quarter of a degree C. The same current was employed in determining the fundamental interval of the thermometers. The heating effect could be safely neglected, as it was nearly

* 'Proc. Inst. C.E.,' 1898.

constant and would not produce an error greater than one-twentieth of a degree C. Owing to slight changes in temperature from stroke to stroke during the working of the gas engine, the mean temperature at any part of the cycle could rarely be observed with an approximation closer than 1° . As the temperatures to be observed were about 100° C., no great refinements in testing the wire were required.

4. *The Periodic Contact-maker and the Electrical Connections.*—In order to observe the temperature at a definite point in the cycle, a periodic contact-maker was inserted, either in the galvanometer or in the battery circuit, and was set to close the circuit at the desired point. In this method errors may arise from thermo-electric or induction effects. Both effects were practically negligible with the apparatus employed, but the thermo-electric effects were rather larger and more variable than the induction effects. The periodic contact was, therefore, usually connected in the battery circuit, so as to eliminate the thermo-electric effects. The electrical connections, including the periodic contact-maker, are shown in fig. 5. In this diagram PS, QS are

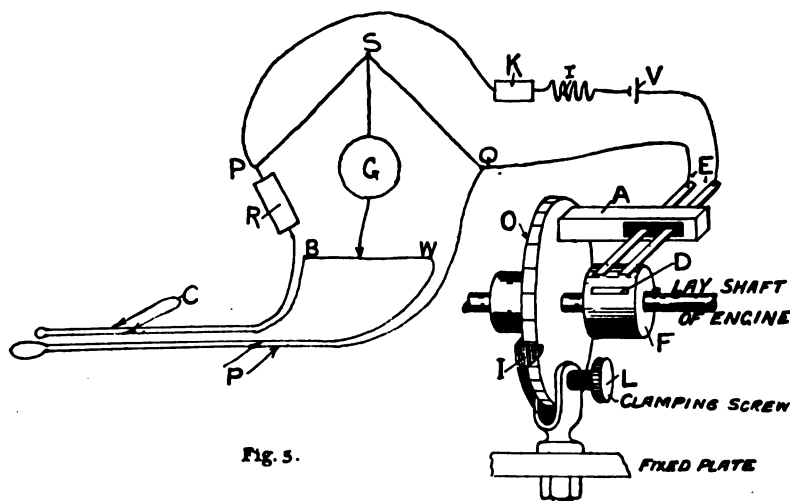


Fig. 5.

the equal ratio arms of the Wheatstone bridge. The galvanometer G is connected to the point S and to the sliding contact on the bridge wire BW. The thermomometer and its leads P are connected on one side of the bridge wire, and the compensator C and the balancing resistance R on the other. The battery circuit includes a mercury reversing key K, an adjustable resistance r , and a storage cell V; and the battery is connected to the bridge at the points P and Q, and to the brushes of the periodic contact-maker at E. The brushes E are carried by an insulated arm A bolted to a divided disc O

riding loosely on the lay shaft of the engine, and capable of being clamped in any position by the screw L. The index I shows the crank angle, corresponding to the middle point of the contact when the insulated copper strip D carried in the fibre bush F passes under the brushes.

5. *Percussion Contact-maker.*—The common form of wipe-contact-maker illustrated in fig. 5 was employed in the earlier experiments, but was found to possess certain disadvantages. The contact was difficult to keep clean and the timing was liable to vary with speed and wear. The duration of contact could not be readily adjusted or accurately verified. In the later experiments a novel form of contact was adopted which appeared to be free from these defects. The construction of this contact-maker is illustrated in fig. 6. A brass bush B keyed to the lay shaft of the engine carries two fibre

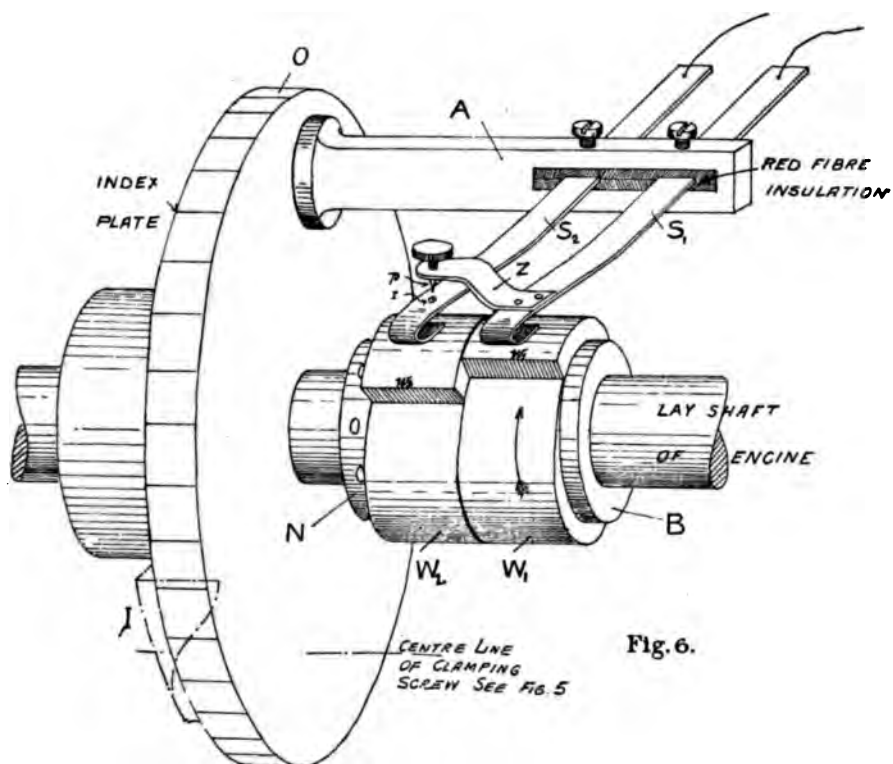


Fig. 6.

washers or cams W_1 and W_2 , which can be clamped in any relative angular position against the flange of the bush by the nut N. A radial step, as w_1 , is made in each washer and the surface gradually rises from the bottom of the step to the normal circular surface of the washer. The brushes of the wipe-contact are replaced by stiff springs S_1 and S_2 , the reflexed ends of which

rest on the fibre cams. A projection Z carrying a platinum-pointed screw p is riveted to one of the springs and the screw p is adjusted so that its point is just clear of the platinum rivet r in the other spring when both springs are riding on the circular surfaces of their respective cams. Contact is made when the rotation of the lay shaft in the direction of the arrow brings the radial step w_1 of the cam W_1 under the spring S_1 , thereby allowing it to fall down the step, thus bringing p and r together. Contact is broken when the radial step w_2 of the cam W_2 reaches the spring S_2 , thereby allowing the second spring to fall down the step w_2 . The epoch and duration of contact are readily adjusted by adjusting the angular positions of the cams relatively to the bush and also with regard to one another. The distance between the springs and the platinum contacts and the steps w are exaggerated in the diagram in order to make the principle of the apparatus clear. The percussion form of contact with platinum points was found to give more definite and certain results than the wipe pattern. It always kept itself clean, and no trouble of any kind was experienced with it. The duration of contact was generally adjusted to correspond with 20 degrees of the crank angle or $1/36$ part of a revolution of the lay shaft.

6. *General Arrangement of the Engine.*—The only engine immediately available for the purposes of the tests was a 10 H.P. Crossley, forming part of the laboratory equipment of the Central Technical College, with a cylinder 7 inches bore and 14 inches stroke, the compression ratio being 4.68. It was not quite the latest pattern, but was in very good condition and well suited for testing the application of the method. It had porcelain tube ignition. It was directly connected to a four-pole dynamo of 8 kw. capacity, mounted on the same shaft. This arrangement was particularly advantageous, as it permitted the engine to be run under widely varying conditions of speed and load. For measuring temperatures by the periodic contact method, it is most important that the cycle of operations should be perfectly regular, and that there should be no missed explosions; otherwise it is impossible to take readings accurately, owing to the wide variations of temperature from stroke to stroke. With this object, the governor was disconnected, and the gas-admission valve arranged to open at every suction stroke. The field of the dynamo was separately excited, and the load taken by adjustable wire resistances, so that the engine could be made to run quite steadily at low speeds if desired. By a slight alteration in the electrical connections it was possible to supply the dynamo with current from the external lighting system, and employ it to drive the engine. This was required in some trials made for the purpose of testing the sensitiveness of the thermometers.

7. *Indicator Diagrams.*—When running the engine with rich mixtures, the

rapidity of the explosion was so great that satisfactory diagrams could not be obtained with the ordinary piston type of indicator. The sudden rise of pressure caused violent oscillations of the pencil, which continued throughout the stroke and made accurate readings impossible. For this reason, an optical indicator, or "manograph," of the Carpentier type was employed, with some modifications suggested by previous experience. In this instrument the pressure acts upon a steel disc or diaphragm, the movement of which is transmitted to a short optical lever, which carries a mirror reflecting a spot of light on to a photographic plate. The lever is pivoted on a fixed point and has a second arm at right angles to the first, which simultaneously receives a movement corresponding with the movement of the piston. This manograph was originally intended for taking diagrams from small high-speed motors with closed crank-chambers. It was supplied with a long, fine copper tube, for connecting the disc chamber to the cylinder, and with a long, flexible coupling to be attached to the crank-shaft, the rotation of which was made to reproduce the motion of the piston by means of a small crank actuating the arm of the optical lever. In adapting the manograph to the gas engine, we found it more convenient to dispense with these connections, which were a source of inaccuracy. The disc chamber was screwed directly on to the indicator cock of the engine. In the earlier experiments the piston motion was obtained from a sprocket wheel on the lay shaft, but later it was reproduced directly by means of a lever driven by a cord attached to the usual indicator rig connected to the piston of the gas engine. Fig. 7 shows the optical indicator in place, and also the sprocket wheel and band driving from the lay shaft. The figure shows incidentally also the general arrangement of the gear for working the admission and the thermometer valves, and the disc and contact-maker on the lay shaft, the details of which have already been illustrated diagrammatically in figs. 4 and 5.

As the pressure scale given by a plane disc is not one of equal parts, and is liable to vary slightly with slight differences in the clamping of the disc, the scale of the indicator was calibrated on each occasion in its actual position on the engine. A gas bottle and a standard pressure gauge were connected to the blow through hole of the indicator cock, and lines were traced on the photographic plate corresponding to equal intervals of pressure, and also lines at right angles to these corresponding to equal displacements of the piston. By using a grill prepared in this manner for measuring the diagrams, errors due to the variation of the pressure scale, or inaccuracy in the reproduction of the piston motion, are practically eliminated. By using discs of different thicknesses, or by different combinations of discs, a considerable range of pressure could be covered with

satisfactory accuracy. For the lower pressures, and for the tests in which the engine was driven by the electric motor without firing, a steam engine indicator of the Crosby pattern was also employed. This indicator was calibrated by weights placed upon a revolving plunger of known area, and

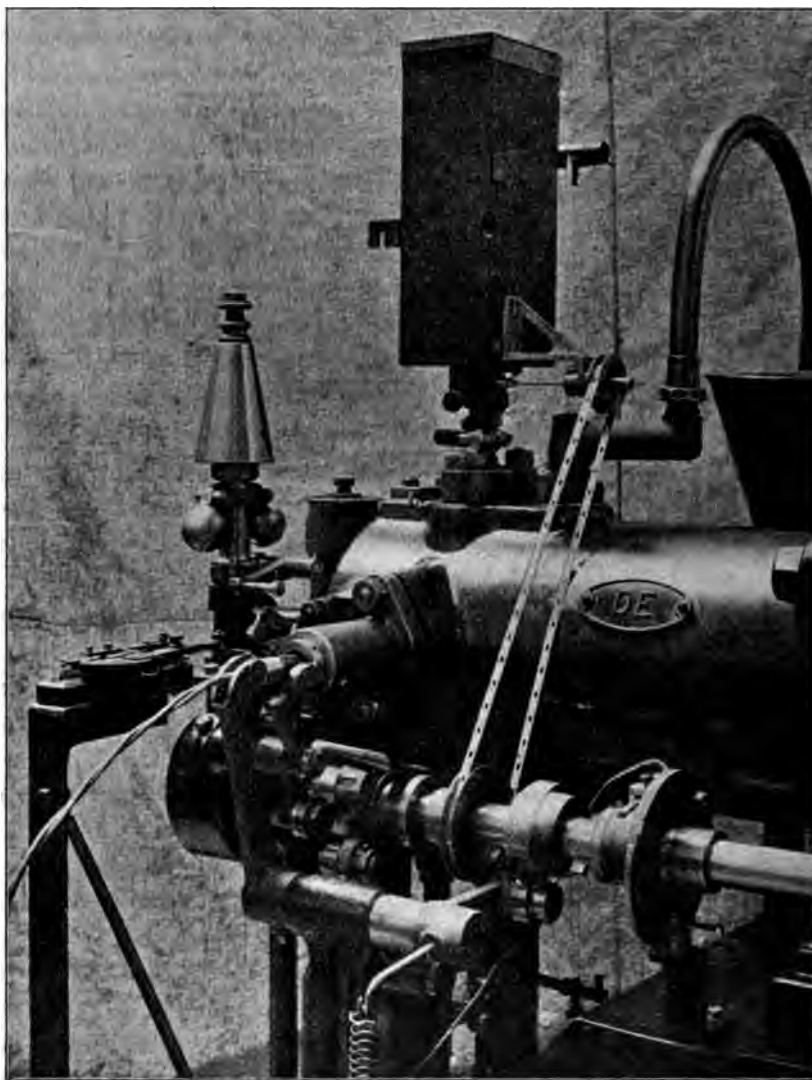


FIG. 7.

was found to be correct and to agree with the optical indicator in those tests in which diagrams were taken with both instruments.

8. *Testing the Platinum Thermometers for Lag.*—It was well known from previous experiments that a platinum wire, 0.001-inch diameter, was capable

of following the cyclical variation of temperature of a gas during suction and compression with sufficient accuracy for the determination of the suction temperature, but it appeared desirable to measure the lag of the thermometer at various speeds under these conditions, and to test whether a thermometer inserted in the manner already described could be relied upon to give the average temperature of the mixture in the cylinder, and how far its readings might be affected by the temperature of the valve in which it was enclosed. For this purpose the engine was driven by a motor, compressing and expanding a charge of air without firing. Temperature readings were taken throughout the cycle for comparison with the mean temperatures deduced from the indicator diagrams.

Two thermometers were employed which differed slightly in the disposition of the platinum loop. In the first, designated Pt_1 , the fine loop was attached in the usual manner, projecting beyond the ends of the leads. In the second, designated Pt_2 , the copper leads were made somewhat longer, and the platinum loop was inverted so as to lie between the leads. It was thought that with this latter method of construction the fine wire loop would be better protected from accidental damage in inserting or withdrawing the thermometer, and would be better able to withstand the shock of opening or closing the thermometer valve. This proved in fact to be the case. It was found, however, that the projecting loop Pt_1 suffered very little distortion, and that although the thermometers agreed very well on the readings of the suction temperature, the readings of Pt_2 were appreciably affected by the close proximity of the leads to the fine wire, when the difference of temperature between the leads and the surrounding gas was considerable.

Two kinds of motor-driven tests were made. In the first kind the gas-cock was shut and the valves were worked in the usual way, so that a fresh charge of air was taken in and compressed during each cycle. In the second kind the gas-cock was shut, the valve levers were removed, and the thermometer valve was fixed permanently open with the gas admission valve permanently closed, and the tension of the exhaust valve spring was relaxed so as to allow it to act as a non-return valve for admitting a little air to the cylinder to compensate for leakage at the end of each suction stroke. Under these conditions the piston expands and compresses a practically constant charge of air at each revolution, and there is little or no disturbance due to the opening and closing of valves. This made it possible to secure a more accurate comparison of the thermometer with the indicated temperatures throughout the cycle, and to obtain a more satisfactory estimate of the lag. With the valves opening and closing in the

ordinary way the cycle occupies two revolutions, and the readings of the thermometer from stroke to stroke are appreciably disturbed by slight variations in the opening and closing of the valves. Moreover, the mass of air contained in the cylinder is constant only for a part of each alternate revolution, so that the comparison with the indicator cannot be extended satisfactorily throughout the cycle.

9. *Comparison of the Temperatures recorded by the Thermometer with the Temperatures calculated from the Indicator Diagram.*—The comparison in the case of the first method of working, namely, valves opening and closing in the usual way, is made in fig. 8. The broken line represents the reading

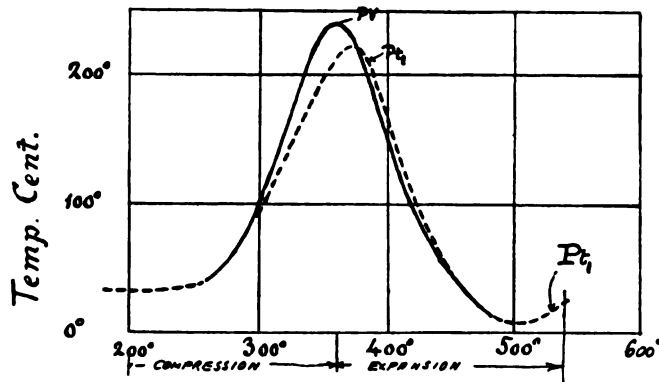


FIG. 8.—Crank Angle from beginning of Suction Stroke.

of the platinum thermometer P_t in degrees Centigrade, plotted with reference to crank angle during the compression and expansion strokes. The full line represents the temperatures deduced from the corresponding indicator diagram by calculating the product PV for the period during which the mass of air enclosed remained sensibly constant. The average speed in this trial was 102 revolutions per minute. An appreciable leakage or loss of heat takes place during the period of maximum compression, so that the compression and expansion curves are not exactly superposed on the card, but each is sensibly adiabatic, following the law $PV^{1.4} = \text{a constant}$ within the limits of error of the pressure measurements. It would make very little difference to the form of the curve between 260 degrees and 460 degrees of crank angle if the temperatures at each point were calculated from the pressures alone (instead of from the product PV), assuming the adiabatic law $\theta^{1.4}/p^{0.4} = \text{a constant}$. The temperatures on the PV curve are calculated on the assumption that the mean temperature of the charge is given correctly by the platinum thermometer at 260 degrees of crank angle. It will be observed that the P_t curve is not quite

symmetrical with the PV curve, the lag appearing greater during compression than during expansion. This may have been caused by some peculiarity in the direction of the currents of air in the cylinder with reference to the position of the ribs of the thermometer valve during compression. The thermometer valve was fixed in this experiment with one of the ribs vertically over the other, so that the opening through the valve might be horizontal or parallel to the axis of the cylinder. During expansion, when the turbulent motion of the air due to admission had subsided, the motion is probably parallel to the axis of the cylinder and the lag of the thermometer is seen to be very small. The PV and Pt curves reunite towards the end of expansion. It was observed in another experiment that the effect of turning the thermometer valve through a right angle, so that the ribs should not obstruct the air current, was to raise the maximum indication 10° C. The reading at the lowest point corresponding with the suction temperature was not appreciably affected by the position of the thermometer valve. In a repetition of this test with the thermometer Pt₂ having the inverted loop, it was found that the close proximity of the copper leads to the fine wire raised the readings of the suction temperature 2° to 3° C. and lowered the reading of the maximum temperature nearly 20° C. It may be inferred from this test that a thermometer of the type Pt₁ with a projecting loop may be trusted to give the suction temperature with an approximation of 1° C., in spite of the presence of the enclosing valve, providing that the temperature of the valve does not differ greatly from that of the mixture in the cylinder. When the temperature is changing most rapidly and the temperature of the valve differs nearly 200° from that of the air, the thermometer lags only 20° and a change in the position of the ribs of the thermometer valve does not affect the readings by more than 10° C.

The comparison in the case of the second method of working, in which the valves are continuously closed, is illustrated in fig. 9. This method promised to afford a more accurate method of testing the thermometer owing to the greater steadiness of the conditions, which permitted more accurate readings of the temperature. Some unexpected difficulties were encountered owing to the presence of small quantities of water, resulting from the formation of fog, but the observations were in many respects instructive, and may be worth recording as additional evidence. The quantity of water required to saturate the clearance space at a temperature of 100° C. was only 0.003 of a pound. Nearly half of this quantity was found to have accumulated in some of the experiments, which afforded an interesting study in the adiabatics of fog. The effect of the formation of fog is very greatly to reduce the range of temperature for a given range of pressure, and the presence of water must,

therefore, be carefully avoided in this method of testing a platinum thermometer. In the test reproduced in fig. 9, the air in the cylinder was sufficiently dry for the calculation of the temperatures from the card by the PV method. The compression and the expansion curves were very nearly symmetrical and adiabatic. The motion of the air in the cylinder was parallel to the axis in both, and the PV and Pt curves were approximately symmetrical. The lag was greater than in fig. 8, partly owing to the higher speed (130 revolutions per minute), but partly also due to the more quiescent

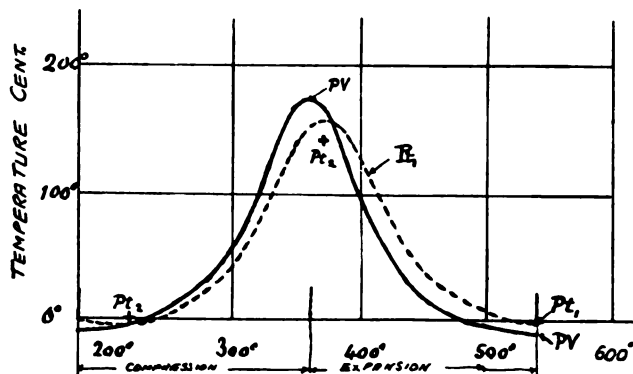


FIG. 9.—Crank Angle from beginning of Suction Stroke.

state of the air in the cylinder. The range of temperature with Pt_1 was from -6° to $+159^{\circ}$ C., as against -10° to $+173^{\circ}$ C., calculated from the card. It must be remembered, however, that there was probably a snow fog in the cylinder at -10° , which throws some doubt on the accuracy of the PV curve and would account for part of the lag of the thermometer owing to condensation on the wire. Also that an error of $1/1000$ of an inch in measuring the card would make an error of 1° of temperature in the PV curve at this point. The range given by the inverted loop thermometer Pt_2 in this test was from 0° C. to 142° C., being reduced by the proximity of the wire leads, the temperature of which was approximately 50° C. The experiment was repeated with and without the thermometer valve in place. The presence of the valve lowered the reading of the platinum thermometer about 10° C. at the point of maximum temperature when the ribs were placed in the horizontal plane so as to obstruct the flow of the air through the aperture, but it did not make any appreciable difference when the aperture was horizontal.

10. *Suction Temperature in Gas Trials.*—A number of trials were run under various conditions of speed and load, and gas supply, with the engine driving the dynamo in the ordinary way. For these trials the thermometer

valve was adjusted to open about the middle of the suction stroke, and close soon after the middle of the compression stroke. The temperatures were observed at the end of the suction stroke, and just after the closing of the admission valve. An observation was also taken at the end of the compression stroke when the thermometer valve was closed in order to give the temperature of the valve itself. The suction temperature was found to vary with the conditions of running from about 95° C. on light load trials to about 125° C. at maximum load, the air temperature being in all cases nearly 20° C., and the jacket temperature 27° C. It should be remembered that in all these trials an explosion occurred at every second revolution, that is, there were no misses, the governor being entirely cut out. The trials were not, however, sufficiently extended to show the dependence of the suction temperature on the various conditions of load and speed and gas supply and jacket temperature. For the present the authors must content themselves with giving an illustration of the method of calculation they propose, reserving further discussion until more complete data are available.

The most interesting of the trials from a theoretical point of view are those with rich mixtures in which combustion is practically complete at constant volume and the diagram conforms most closely to the theoretical type. A typical example is shown in fig. 10, taken from trial 26, photo 62. Six consecutive explosions, photographed on the same plate, were practically identical. The following are the data of this trial:—

Revolutions per minute, 130 ;
Ratio of gas to air, 1 to 7.1 ;
Atmospheric temperature, 20° C. ; jacket temperature, 27° C. ;
Temperature of thermometer valve at 360 degrees crank angle, 122° C. ;
Temperature of mixture in cylinder at 260 degrees crank angle, 111° C. ;
Pressure in pounds per square inch absolute at 260 degrees crank angle, 18.5 ;
Volume of mixture at 260 degrees crank angle, 0.2846 cubic feet.

In calculating the temperatures along the expansion line, it is assumed that combustion is complete, and that the gases have undergone a molecular contraction, depending upon the richness of the mixture and the composition of the gas, which in this case amounts to 4.3 per cent. To find the temperature at any point in the expansion curve it is only necessary to divide the product of the pressure and volume at that point by the constant 0.01315, representing the observed value of the product pv/T at the point corresponding to 260 degrees crank angle λ , corrected for contraction. The resulting curve of temperature is shown in the upper part of the diagram (fig. 10). The temperature thus calculated is the apparent or effective

temperature, and includes the effect, if any, of dissociation. By comparing and analysing such curves it may be possible to deduce important relations bearing on the phenomena of combustion of gaseous mixtures. The curve shown in the diagram exhibits a marked change of curvature at 0.4 of the

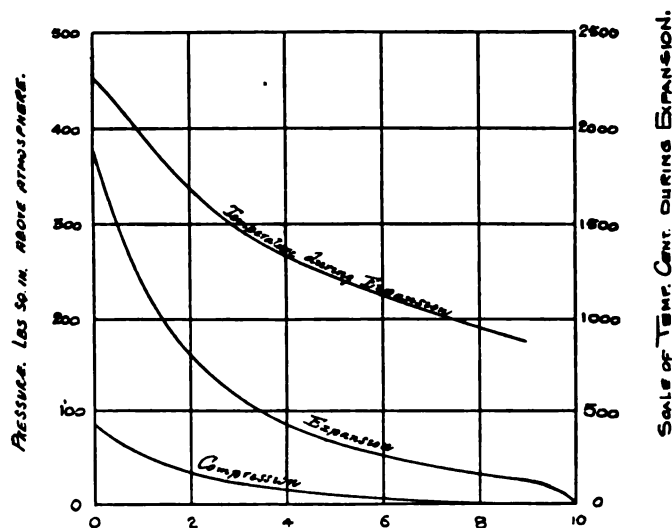


FIG. 10.—Trial 26. Diagram Photo 62.

stroke, and becomes nearly straight. A peculiarity of this kind might be due to some imperfection of the indicator, but it might also imply a final stage in the combustion. Without an exact knowledge of the temperature it would be impossible to investigate such points satisfactorily.

By a curious coincidence a diagram taken in another trial, fig. 11, shows

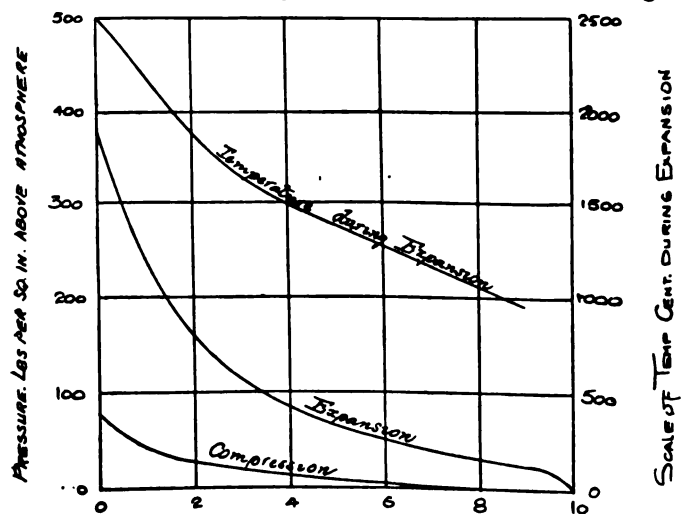


FIG. 11.—Trial 4. Diagram Photo 9.

photo 9, with a different ratio of gas to air, namely 1 to 5·8, gave a practically identical expansion curve, not differing by more than 1 pound at any point from the curve of the preceding example recorded on photo 62. The mean pressures deduced from the brake horse-power were also very nearly identical. Without a knowledge of the suction temperature it might be inferred that the two trials were really identical and that some mistake had been made in the gas measurements. The data for this trial are as follows:—

Revolutions per minute, 114. Ratio of gas to air, 1 to 5·8.

Atmospheric temperature, 21° C. Jacket temperature, 27° C.

Temperature of mixture at 260 degrees crank angle, 130° C., and pressure 17·8 lbs. per square inch absolute.

Molecular contraction on combustion, 5·1 per cent.

The constant for calculating the temperature along the expansion curve comes out 0·01195 in place of 0·01315, and the temperatures are all much higher, as they should be with a richer mixture. The temperature curve in fig. 11 shows the same curious anomaly as that from photo 62 in fig. 10, although the diagram was taken with a different disc having a different pressure scale, and with an entirely different arrangement of indicator gear, the piston motion being transmitted from the lay shaft in the way shown in fig. 7, instead of being taken direct from the usual indicator rig as was the case in Experiment 26.

11. *Conclusions.*—It appears probable from these experiments that the temperature of the thermometer valve never differs very much from the temperature of the gases shortly after the closing of the admission valve in the method of construction adopted by the authors, in which the thermometer valve is inserted through the spindle of the admission valve. In a specially designed gas engine, a separate opening might be provided for the insertion of the thermometer, but it is probable that the temperature of the valve in this case would not be so nearly equal to the suction temperature to be measured. The method adopted by the authors has the advantage that it can be applied without difficulty to any existing engine by simply making a special admission valve. Since the temperature of the thermometer valve in this method of construction differs so little from the suction temperature at the required point, it appears probable that the thermometer gives the actual suction temperature required with an approximation of the order of 1° C. The temperature at this point can probably be measured with a fine wire with a greater degree of accuracy than the pressure. In order to obtain the pressure at this point, it is necessary to take a diagram

with a light spring in the indicator, as the pressure cannot be satisfactorily measured with a spring strong enough to record the explosion temperature. Further, it is absolutely necessary in these investigations that the engine should repeat a perfectly regular cycle at each explosion. No results of any value can be obtained with a hit-and-miss governor in operation, because the conditions vary too greatly from stroke to stroke. This has been repeatedly shown by previous trials. In measuring the expansion and exhaust temperatures by a similar method, it would be most appropriate so far as the temperatures to be measured are concerned to insert the thermometer valve through the spindle of the exhaust valve.

The authors desire to record their obligation to Mr. Witchell and Mr. Betterley and to other members of the Laboratory staff for the able assistance they severally gave during the investigation.

On the Normal Weston Cadmium Cell.

By F. E. SMITH, A.R.C.Sc.

(Communicated by R. T. Glazebrook, F.R.S. Received July 13,—
Read November 21, 1907.)

(From the National Physical Laboratory.)

(Abstract.)

The experimental investigations described had as their primary object the improvement of the Clark and cadmium cells as standards of electromotive force.

In the past many investigators have pointed out that the mercurous sulphate used as a depolariser may produce variations in the E.M.F. as great as 0.002 volt, and the first thing sought by us was a mode of manufacture of the sulphate which could be relied on to give a constant product. We have prepared the salt in four ways: (1) Electrolytically (the method is due to Carhart and Hulett, and Wolff); (2) by chemical precipitation, mercurous nitrate being added to sulphuric acid; (3) by the recrystallisation of purchased samples of mercurous sulphate from strong sulphuric acid; and (4) by the action of fuming sulphuric acid on mercury. The mean value of the cells set up with the electrolytic salt is 1.01828 volts;* with the sulphate prepared by (2) the E.M.F. is 1.01830 volts; (3) gives 1.01832 volts, and (4) gives 1.01831 volts. We conclude that the mode of manufacture of the depolariser is immaterial, provided that certain conditions are observed, and our guiding principle in the manufacture of the salt and the preparation of the paste is to prevent hydrolysis by keeping the salt in contact with dilute sulphuric acid (1 to 6) or with saturated cadmium sulphate solution.

The effect of the size of the crystals of the depolariser, to the importance of which attention has been called by H. v. Steinwehr, was investigated by using crystals of various sizes and measuring the E.M.F. of the cells in which they were inserted. Twenty samples of the salt were examined under the microscope, and in 12 cases microphotographs were taken, the magnification being 250. The uniformity in the size of the crystals is most marked in samples prepared by method (2), and this is recommended as a standard method of preparation of the salt. In general, the crystals varied in size from 5 to 30 microns, and we conclude that no large crystals of mercurous

* The E.M.F. is given in terms of the ampere (10^{-1} C.G.S., measured by the Ayrton-Jones ampere balance) and the international ohm.

sulphate which are sufficiently soluble to act as an efficient depolariser can give an E.M.F. appreciably lower than that due to crystals from 5 to 30 microns long.

A very large proportion of the cells dealt with have not varied in E.M.F. by more than two parts in 100,000 since the first month of their preparation, and some of the cells are nearly three years old. A few abnormal cells have fallen in E.M.F. by about 25 parts in 100,000, but the depolariser in these is of a peculiar colour and suggests hydrolysis of the salt.

The recuperative power of the cadmium cell was tested by short-circuiting different cells for 1 minute, 5 minutes, 5 hours, and 5 days. The recovery in each case was very rapid.

The lag of E.M.F. with temperature is very small, and the temperature coefficient for the range, 10° C. to 30° C., is given by the following equation :—

$$E_t = E_{17} - 3.4 \times 10^{-5}(t-17) - 0.066 \times 10^{-5}(t-17)^2.$$

This is in very good agreement with the formula given by the Reichsanstalt.

The Silver Voltameter.

Part I.—By F. E. SMITH, A.R.C.Sc., and T. MATHER, F.R.S.

Part II.—By F. E. SMITH, A.R.C.Sc., and T. M. LOWRY, D.Sc.

(Communicated by R. T. Glazebrook, F.R.S. Received July 22,—
Read November 21, 1907.)

(From the National Physical Laboratory.)

(Abstract.)

PART I.—*On a Comparison of many Forms of Silver Voltameters.* By F. E. SMITH; and *a Determination of the Electrochemical Equivalent of Silver.* By F. E. SMITH and T. MATHER, F.R.S.

It has been known for several years that the measurement of electric quantity by the deposition of silver is liable to inaccuracies which appear to be dependent on the size and nature of the anode and cathode and on the electrolyte of the voltameter employed. Hence the necessity of an enquiry to ascertain the possibility of specifying a voltameter which is easily reproducible and in which an ampere-second always deposits the same mass of silver.

In some very early experiments it was found that the mass of the deposit was dependent on the mode of preparation of the silver nitrate, but on several crystallisations of the salt constant results were obtained.

Very large voltameters were experimented with. Four of the cathode bowls had a capacity of 500 c.c. each, and in general from 300 to 400 c.c. of electrolyte were employed. The anodes were coated with electrically-deposited silver.

With a Rayleigh form of voltameter containing an electrolyte of pure silver nitrate 52 determinations of the electrochemical equivalent were made, the current being indirectly measured by the British Association (Ayrton Jones) ampere balance. The mean of the 52 determinations was 1.11827 milligrammes per coulomb, and the mean difference was 2.4 parts in 100,000. With a Richards form of voltameter, in which the anode liquid was separated from the cathode liquid by a porous pot, variable results were at first obtained, but this was found to be due to the presence of acid in the pots. When the pots were baked in an electric furnace before their employment in a voltameter, constant values resulted, and the mean of these was 1.11828 milligrammes per coulomb, *i.e.*, practically identical with that obtained with the Rayleigh form. Richards originally obtained a difference of eight

parts in 10,000 between the two forms, his form giving the smaller deposit; later he found the difference to be four parts in 10,000, and recently van Dijk has found a difference of half this latter amount. Further observations were made with a syphon and other modified forms of voltameter, and the same value, 1.11827, was found, pointing to little or no irregularities in the large-size Rayleigh form of voltameter. Deposits were made when the voltameter was subject to a gaseous pressure of 2.4 cm. of mercury, and were found to be identical with those made under a pressure of 1 atmosphere. We have thus failed to confirm the observations of Schuster and Crossley and of Kahle. At a temperature of 90° C. we found the deposits to be very slightly heavier than at 15° C., but the calculated temperature coefficient was so small (1×10^{-6}) that we believe the increase to be due to the action of the filter paper on the silver nitrate, as originally suggested by Kahle.

The range in the current intensities was from 0.5 ampere to 8 amperes, and for this range we found no appreciable irregularity.

We conclude that the Rayleigh form of voltameter as employed by us is reproducible to one or two parts in 100,000, and that the electrochemical equivalent of silver is 1.11827 milligrammes per coulomb.

PART II.—*The Chemistry of the Silver Voltameter.* By F. E. SMITH, A.R.C.Sc., and T. M. LOWRY, D.Sc.

Before a definite value could be assigned to the electrochemical equivalent of silver it was necessary to demonstrate the possibility of preparing again and again, from silver nitrate of different origins, solutions which should give identical weights of silver when electrolysed under identical conditions. We prepared silver nitrate from electrolytic silver, from much used silver nitrate, and from commercial samples of the salt, and satisfied ourselves that by taking precautions in recrystallising, etc., a sufficiently constant product could be obtained. Tests on commercial silver nitrate were gratifying in so far that with one exception all the samples (eight in all) examined gave figures agreeing with those obtained from the samples which were specially prepared, and we conclude that, except in measurements of high precision, the commercial salt may be used without purifying.

Attempts to confirm the observations of Novak, Rodger and Watson, Kahle, van Dijk and others, on the effect of repeated electrolysis of a solution, show that in our voltameters there may be a very small increase in the deposit with continued use of a solution, but nothing comparable with that obtained by the observers mentioned. We also fail to confirm the formation, at the anode, of a complex silver salt, giving rise to

heavy deposits at the cathode, as suggested by Rodger and Watson and by Richards.

High values are obtained for the electrochemical equivalent if the solution contains oxide, carbonate, chloride, nitrite or hyponitrite. Low values are caused by acid. The impurities which raise the electrochemical equivalent appear to be those which are insoluble in water but soluble in silver nitrate solutions; they are, therefore, precipitated from the impoverished solution at the cathode.

There may be slight changes in the electrolyte due to its interaction with filter paper, but the mass of the deposit is not seriously affected thereby in our size of voltameter in the course of one electrolysis. It is inadvisable, however, in measurements of high precision to use an electrolyte more than once.

Silver chlorate and silver perchlorate appear to give normal deposits, but are more troublesome in use and have no advantage over the nitrate.

The Diurnal Variation of Terrestrial Magnetism.

By ARTHUR SCHUSTER, F.R.S.

(Received October 31,—Read November 7, 1907.)

(Abstract.)

1. In a previous communication* I proved that the diurnal variation of terrestrial magnetism had its origin outside the Earth's surface, and drew the natural conclusion that it was caused by electric currents circulating in the upper regions of the atmosphere. If we endeavour to carry the investigation a step further, and consider the probable origin of these currents, we have at present no alternative to the theory, first proposed by Balfour Stewart, that the necessary electromotive forces are supplied by the permanent forces of terrestrial magnetism acting on the bodily motion of masses of conducting air which cut through its lines of force. In the language of modern electrodynamics, the periodic magnetic disturbance is due to Foucault currents induced in an oscillating atmosphere by the vertical magnetic force. The problem to be solved in the first instance is the specification of the internal motion of a conducting shell of air, which shall, under the action of given magnetic forces, determine the electric currents producing known electromagnetic effects. Treating the diurnal and semi-diurnal variations separately, the calculation leads to the interesting results that each of them is caused by an oscillation of the atmosphere which is of the same nature as that which causes the diurnal changes of barometric pressure. The phases of the barometric and magnetic oscillations agree to about $1\frac{1}{2}$ hours, and it is doubtful whether this difference may not be due to uncertainties in the experimental data. In the previous communication referred to, I already tentatively suggested a connection between the barometric and magnetic changes, but it is only recently that I have examined the matter more closely. In the investigation which follows, I begin by considering the possibility that both variations are due to one and the same general oscillation of the atmosphere. The problem is then absolutely determined if the barometric change is known, and we may calculate within certain limits the conducting power of the air which is sufficient and necessary to produce the observed magnetic effects. This conducting power is found to be considerable. It is to be observed, however, that the electric currents producing the magnetic variations circulate only in the upper layers of the atmosphere, where the pressure is too small to affect the barometer; the two variations have their origin,

* 'Phil. Trans.,' A, vol. 180, p. 467 (1889).

therefore, in different layers, which may to some extent oscillate independently. Though we shall find that the facts may be reconciled with the simpler supposition of one united oscillation of the whole shell of air, there are certain difficulties which are most easily explained by assuming possible differences in phase and amplitude between the upper and lower layers. If the two oscillations are quite independent, the conducting power depending on the now unknown amplitude of the periodic motion cannot be calculated, but must still be large unless the amplitude reaches a higher order of magnitude than we have any reason to assume.

The mathematical analysis is simple so long as we take the electric conductivity of the air to be uniform and constant; but the great ionisation which the theory demands requires some explanation, and solar radiation suggests itself as a possible cause. Hence we might expect an increased conducting power in summer and in day time as compared with that found during winter and at night. Observation shows, indeed, that the amplitude of the magnetic variation is considerably greater in summer than in winter and we know that the needle is at comparative rest during the night. The variable conducting power depending on the position of the sun helps us also to overcome a difficulty which at first sight would appear to exclude the possibility of any close connection between the barometric and magnetic variations; the difficulty is presented by the fact that the change in atmospheric pressure is mainly semi-diurnal, while the greater portion of the magnetic change is diurnal. This may, to some extent, be explained by the mathematical calculation, which shows that the flow of air giving a 24-hourly variation of barometric pressure is more effective in causing a magnetic variation than the corresponding 12-hourly variation, but the whole difference cannot be accounted for in this manner. If, however, the conductivity of air is greater during the day than during the night, it may be proved that the 12-hourly variation of the barometer produces an appreciable periodicity of 24 hours in the magnetic change, while there is no sensible increase in the 12-hourly magnetic change, due to the 24-hourly period of the barometer. The complete solution of the mathematical problem for the case of a conducting power proportional to the cosine of the angle of incidence of the sun's rays is given in Part II. But even this extension of the theory is insufficient to explain entirely the observed increased amplitude of the magnetic variation during summer. We are, therefore, driven to assume either that the atmospheric oscillation of the upper layer is greater in summer than in winter and is to that extent independent of the oscillation of the lower layers, or that the ionising power of solar radiation is to some extent accumulative and that the atmospheric conductivity is, therefore, not com-

pletely determined by the position of the sun at the time. The increased amplitude at times when sunspots are frequent is explained by an increased conductivity corresponding to an increase in solar activity. All indications, therefore, point to the sun as the source of ionisation, and ultra-violet radiation seems to be the most plausible cause.

A good test of the proposed theory may be found in a closer examination of the diurnal magnetic changes in the equatorial regions, because, owing to the inclination of the magnetic to the geographical axis, the magnetic changes ought to have a term which does not depend on local time, but on the time of the meridian containing the geographical and magnetic pole. This term has its greatest importance at the equator and at the time of the equinox. A study of the lunar effects may also lead to interesting conclusions, as, according to the point of view of the present paper, they must be explained by some tidal oscillation.

The value of the conductivity necessary to explain the diurnal variation in the manner indicated depends on the thickness of the layers which carry the currents. If e be the thickness and ρ the conductivity and the amplitude of oscillation in the upper layers is assumed to be the same as that deduced from the barometric variation, it is found that $\rho e = 3 \times 10^{-6}$. If e is equal to 300 kilometres, the conductivity would have to be as high as 10^{-13} , while the observed conductivity of air at the surface of the earth under normal conditions is of the order 10^{-24} ; at a height at which the pressure is reduced to one degree per square centimetre, the conductivity would be 10^{-18} , assuming the rate of recombination to be independent of temperature, and the ionising power to be the same. This calculation is based on the assumption that the ions conveying the current are identical with those we observe at high pressures, while it is of course possible that the ionic velocities are much greater. But taking all these possibilities into account, we are led to the conclusion that there must be a powerful ionising agent giving a high conductivity to the upper layer of the atmosphere.

If the fundamental ideas underlying the present enquiry stand the test of further research, we are in possession of a powerful method which will enable us to trace the cosmical causes which affect the ionisation of the upper regions of the atmosphere and which act apparently in sympathy with periodic effects showing themselves on and near the surface of the sun.

Results of the Interaction of Mercury with Alloys of other Metals.

By J. W. MALLET, F.R.S., University of Virginia.

(Received August 27,—Read November 21, 1907.)

It is well known that alloying metals with each other often modifies in a remarkable way their several relations to acids and other non-metallic reagents. Examples of this are afforded by the addition of silver to platinum, rendering the latter soluble, along with the former, in nitric acid—by the great resistance to the action of *aqua regia* on platinum when alloyed with rhodium or iridium—and by the solubility in cold, somewhat dilute sulphuric acid, of copper in alloy with nickel and zinc as common “German silver.”

It seemed interesting to see what the behaviour of fluid metallic mercury would be in relation to alloys of metals solid at common temperatures. For instance, if an alloy of two metals—one of them when alone amalgamating readily with mercury and the other not—should be exposed to the action of mercury, would the former resist amalgamation or the latter be rendered amalgamable, or would each continue to behave as though the other were absent and the mercury take up the one and leave the other intact?

Some experiments of this kind, recently made, seem worth recording, as little or nothing bearing upon the question appears in the principal handbooks of chemistry.

It suggested itself first to examine the case of an alloy of two metals presenting evidence of chemical combination between them, not merely of solid solution. Such a case is that of the alloy of tin and platinum which is produced by fusing the two together, the act of union being attended with sudden and very great elevation of temperature, exhibiting brilliant incandescence, and the product being found to have completely changed in respect to cohesion, the two thoroughly malleable metals giving rise to a highly brittle alloy easily crushed to powder.

Tin-platinum Alloy.

For about 5 grammes of platinum in the form of rather thick foil a piece of pure tin was weighed off representing a trifling excess over the quantity needed for two atoms of tin to one of platinum, this excess being intended to allow for a slight loss of tin by oxidation. The tin was closely wrapped in the platinum foil, and the whole was rapidly heated by a blast-lamp flame.

Complete fusion took place in a moment, with vivid incandescence. The button of alloy, after cooling, was moderately hard, very brittle, and easily reduced to powder in an iron mortar. It contained: platinum, 45.26 per cent.; tin, 54.74 per cent.

The specific gravity of the button, taken before crushing, was found to be but 10.72, notably below the calculated value, so that if there were no cavities—none were observed on crushing—there must have been considerable expansion in the act of union of the metals.

The finely pulverised alloy, with about five times its weight of pure mercury, was at once placed in a stoppered glass cylinder, and the vessel was vigorously shaken from time to time for several days. No sign of amalgamation appeared. The larger part of the mercury was run off from the seemingly quite unaltered powder, carefully freed from any trace of the latter by skimming, and distilled at a temperature a little below the boiling point in a hard glass tube, sweeping away the vapour by a current of air produced by a jet pump. No visible residue was left, so that the tin had been completely protected by the platinum from amalgamation, and neither metal had gone into solution. The surface of the particles of the original alloy powder showed under the microscope no sign of adhering mercury.

On treating this unaltered powder of the platinum-tin alloy with another portion of mercury to which a very little metallic sodium had been added, amalgamation took place at once, and the amalgam began to adhere to the surface of the glass vessel. The soft amalgam thus formed seemed to contain entangled in it the larger part of the powder, but very little was present in true solution, as on straining off the fluid portion through chamois leather and distilling, only a trifling residue was obtained, containing but a few milligrammes of platinum and tin. The main mass of the buttery amalgam left behind on straining through the leather was treated with moderately diluted nitric acid until all action ceased. It left undissolved pulverulent grey platinum, and a heavy, finely granular residue, of crystalline appearance under the microscope, greyish white and with metallic lustre. This latter was an alloy of platinum and tin which, like the bulk of the original fused alloy, was not acted upon by mercury. Heated in a stream of dry chlorine gas, it gave off tin as chloride and left metallic platinum, weighings showing the composition to be: platinum, 48.08 per cent.; tin, 51.92 per cent.; agreeing pretty well with the not very probable formula Pt_4Sn_7 , which requires platinum, 48.33 per cent.; tin, 51.67 per cent. It is by no means certain that this material was homogeneous.

It would seem that even in an amalgam which as a whole is liquid and

mobile, the mass may be viewed as consisting of a solid part or phase—the solid metal moistened by mercury—and a liquid part or phase—mercury holding the solid metal in solution—these parts mechanically separable by straining, or often simply by gravity on standing at rest. In the material just referred to nearly all of the tin and platinum seems to have existed in the former of these states.

Silver-platinum Alloy.

Platinum as heavy foil and pure silver ("proof silver" of the United States Mint) were weighed off in proportions representing four atoms of silver and one of platinum, and fused together in an assay crucible at a temperature high enough to render the alloy perfectly fluid. The ingot which was somewhat hard, but quite malleable, was rolled out to strips not more than about a tenth of a millimetre in thickness. These strips weighing about 12 grammes, were cut up into small bits, washed well with ether to remove any traces of oil from the rolls, dried, put into a stoppered glass cylinder, and shaken with about five times their weight of pure mercury, the vigorous shaking being repeated at intervals for several days. The mercury began almost at once to wet the surface of the solid alloy, and after a few hours practically all running mercury had been soaked up and the strips began to crumble. About half as much more mercury was added, and in three or four days an apparently smooth buttery amalgam had been formed.

Almost from the first the amalgam began to adhere with remarkable firmness to the surface of the glass, and before long the whole interior surface of the cylinder was coated with a mirror-like deposit as perfect as that usually obtained by means of silver reduced by aldehyde or Rochelle salt, and remarkably persistent.

The perfectly smooth buttery amalgam, containing no visibly solid fragments of the strips of alloy, was strained by squeezing through chamois leather.

The solid part which was left behind hardened somewhat on standing, but not nearly as much as amalgam of silver alone, and showed some tendency to crumble. Applied to the surface of clean platinum foil it at once produced amalgamation of the latter.

A specimen of simple silver amalgam was strained through chamois leather, and the pasty solid residue was in like manner applied to the surface of clean platinum foil. At first, even with rubbing, no sign of amalgamation of the foil appeared, but on leaving the lump of silver amalgam resting on the surface for an hour or two and then sliding it to one side, a mark was

left showing where the amalgam had lain, and after 24 hours there was distinct amalgamation of the surface. This increase of adhesiveness given to mercury by the presence of silver displays an interesting additional bit of parallelism between silver and the alkaline metals. Removing the lump of amalgam and rubbing the surface of the platinum foil vigorously with a cloth, there was left a visible stain, which changed somewhat in lustre but did not disappear on heating to low redness, showing that silver as well as mercury had adhered to the surface. Whether this silver had been carried down into the platinum by the amalgamation (as is most probable) or was partially alloyed with it by the heating to drive off mercury, the stain did not entirely disappear on treatment with nitric acid.

About 30 grammes of the fluid part of the amalgam from the silver-platinum alloy, which had been strained through chamois leather, was carefully distilled in a stream of air, keeping somewhat below the boiling point to avoid any mechanical loss by spattering, and left behind 60 milligrammes of solid residue. This was "parted" by repeated boiling with concentrated sulphuric acid. The results of the parting show the following comparison between the composition of the original silver-platinum alloy and of this portion of it which had been taken into solution by the mercury :—

| | Original alloy. | Dissolved by mercury. |
|----------------|--------------------|--------------------------|
| Platinum | 31·09 | 18·78 |
| Silver..... | 68·91 | 81·22 |

It thus appears that, unlike the case of the tin-platinum alloy, in which the platinum prevented the tin being amalgamated, in the silver-platinum alloy the silver brings about solution of the platinum by mercury, although in smaller proportion than that in which it was present in the original alloy.

Copper-tin Alloy.

It seemed desirable, in the third place, to see what effect, if any, upon amalgamation would be produced by alloying two metals, each of which is by itself readily taken up by mercury ; and such metals were selected as we have reason to believe, from the experiments of Sir William Ramsay and others, are simply dissolved by mercury, and in the condition of monatomic molecules.

With this in view, a specimen of good speculum metal, made with two parts of copper and one of tin, and hence near Cu_2Sn in composition, extremely brittle, was reduced to very fine powder in an iron mortar ; 10 grammes of this was placed in a stoppered glass cylinder, about five times as much pure

mercury added, and the whole well shaken at intervals for several days. At first there was no sign of amalgamation, but in a few hours this began to appear, and at the end of 24 hours the greater part of the solid alloy had been taken up by the mercury. There was no adhesion of amalgam to the surface of the glass. About half as much more mercury was added, and after four or five days, with many shakings, there remained but a very little solid alloy in powder. This was carefully removed from the surface of the seemingly smooth, buttery, or thickly fluid amalgam, and the latter squeezed in chamois leather. Forty or fifty grammes of the fluid portion which had passed through the pores of the leather was carefully distilled, guarding against spattering. It left but 2 or 3 milligrammes of solid residue, in which both copper and tin were present, the former probably in rather larger proportion than in the original alloy, but the quantity of residue was too small for an accurate analysis.

The pasty amalgam which was retained by the leather showed a strong tendency to crumble, and when examined with the microscope showed numerous particles of the solid speculum metal which had not fully blended with the mercury.

It is evident, therefore, that alloying these two metals—copper and tin—together, greatly diminishes the readiness and extent with which they unite with mercury when they are separately exposed to its action.

On the whole, these experiments show that the relations of mercury to alloys are not the same—at any rate for those tried—as to the component metals taken separately.

Many other experiments of the general nature of those now recorded suggest themselves as worth trying. Thus it would be well to examine the behaviour towards mercury of solid alloys, including one of the alkaline metals, the amalgams of which are so peculiar in character, to try the effect of mercury upon two or more alloys of the same metal in widely different proportions, and to extend such experiments to more complex alloys containing three, four, or a larger number of solid metals.

A Method of Depositing Copper upon Glass from Aqueous Solutions in a Thin Brilliantly Reflecting Film, and thus producing a Copper Mirror.

By F. D. CHATTAWAY, F.R.S.

(Received September 26,—Read November 21, 1907.)

Many organic substances which undergo oxidation easily are able to reduce various metallic oxides. The oxygen is removed with very different degrees of readiness and the property is in consequence often used as a means of recognising particular compounds or atomic groupings.

Silver oxide is especially easily reduced, and if it is dissolved in an aqueous solution of ammonia the metal, by an appropriate agent, as Liebig first observed,* may be obtained attached to the glass walls of the containing vessel as a brilliant reflecting film.

This observation has received an important industrial application in the manufacture of mirrors, and silver thus deposited has now practically replaced the tin amalgam formerly used, which so often seriously affected the health of the workers.

With the view of improving the processes originally used, many chemists have studied the conditions under which glass is coated with silver, but their investigations have generally had for their object the preparation of a liquid which would deposit a uniform and coherent layer of the metal over a large glass surface at the ordinary temperature. Liebig† was the first to solve the problem satisfactorily and his method, in which milk sugar is the reducing agent, was formerly extensively used.

Other metals are not so easily laid down upon glass in a firm reflecting film as is silver; and in particular copper, which is so closely related to it, is not in similar circumstances so deposited. Metallic copper has been attached to glass in various ways. Faraday,‡ about the time when silver mirrors were attracting much attention, made the interesting observation that a mirror-like deposit of the metal upon glass having the proper metallic lustre and colour by reflection, could be obtained by dissolving a little oxide of copper in olive oil and heating plates of glass in a bath of this liquid up to the decomposing temperature of the oil. Mirrors, however, obtained by Faraday's method, if of any size, are liable to be stained and discoloured in patches by

* 'Annalen,' 1835, vol. 14, p. 133.

† 'Annalen,' 1856, vol. 98, p. 132.

‡ 'Phil. Trans.,' 1857, p. 145.

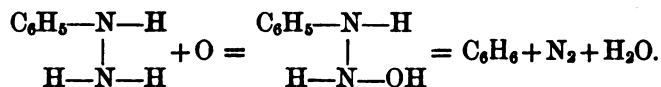
decomposition products of the oil and they are, moreover, generally lacking in brilliancy. Further, as the deposition of the metal only takes place at a temperature above that at which the oil decomposes, the process is excessively disagreeable to carry out and, as the oil is spoiled, it is somewhat costly.

Faraday also discovered* that a fine deposit of copper upon glass could be produced by deflagrating the metal in the neighbourhood of the glass by a Leyden battery in an atmosphere of hydrogen, and Wright, employing a method essentially the same,† obtained small brilliant mirrors of copper on the inner surface of exhausted glass tubes by passing through them an electric discharge between copper electrodes.

Everyone who has reduced Fehling's solution with excess of grape sugar must have noticed that occasionally the metal produced adheres to the sides of the beaker or flask in somewhat reflecting patches, and much brighter patches are obtained when certain copper salts such as formate or acetate are heated in glass vessels. The firm of Weisskopf, in Morchenstein, has further succeeded in depositing copper upon glass by reducing the hydroxide in presence of zinc chloride together with gold or platinum chloride by a somewhat complicated liquid mixture containing cane sugar, glycerine, and formaldehyde.

These facts lead to the conclusion that copper should be capable of deposition in the same way as silver, if a suitable reducing agent were forthcoming; this I have recently found in phenylhydrazine.

Phenylhydrazine, as I have elsewhere shown,‡ especially in presence of caustic potash, which greatly accelerates the action, is easily oxidised by free oxygen, there being produced in all likelihood hydroxyphenylhydrazine, which immediately breaks down into a molecule of benzene, a molecule of nitrogen, and a molecule of water thus:—



Copper oxide acts similarly upon the base, and under suitable conditions the metal can be deposited upon glass in the form of a fine mirror.

The operation may be carried out in a variety of ways, using finely divided black copper oxide suspended in a boiling saturated solution of phenylhydrazine or a liquid made by mixing the latter with a solution of copper hydroxide in alkaline tartrates or ammonia.

* 'Phil. Trans.,' 1857, p. 154.

† Silliman, 'Amer. Journ.,' 1877, [3], vol. 13, p. 49.

‡ 'Trans. Chem. Soc.,' 1907.

The following procedure, which resembles that employed in silvering glass, gives a uniformly excellent result. Heat a mixture of one part of freshly distilled phenylhydrazine and two parts of water till a clear solution is obtained. To this add about half its bulk of a warm saturated solution of cupric hydroxide in strong ammonia. Nitrogen is freely evolved during the addition, and the cupric is reduced to cuprous hydroxide, which remains dissolved in the ammoniacal liquid, and does not undergo any immediate appreciable further reduction until heated. Add next a hot 10-per-cent. solution of potassium hydroxide until a slight permanent precipitate of cuprous hydroxide is produced. If this colourless or pale yellow liquid be cautiously heated in contact with a perfectly clean glass surface, metallic copper is deposited upon it in the form of a thin, coherent, perfectly reflecting lamina.

As nitrogen is evolved during the reduction, and as tarry bye-products are formed in small quantity and float with the benzene produced to the surface of the liquid, if flasks or tubes are to be coppered, devices have to be adopted to keep the inner surface completely covered by the liquid from which the metal is being deposited, whilst allowing the gas to escape.

If the glass in any part is not perfectly coated, the process may be repeated, but a uniform deposit is seldom obtained unless the whole surface is covered in one operation. To obtain a film of sufficient thickness to be permanent, and to prevent its superficial oxidation, it is best to allow it to remain for an hour or so in contact with the warm reducing fluid, and not to pour this off till it has cooled to the temperature of the air. The surface of the deposited copper should then be well washed, first with water and afterwards with alcohol and ether, and finally should be protected from the slow oxidising action of the air by one or two coats of some quick-drying varnish.

Very little of the phenylhydrazine is actually used up in the reduction, and the same fluid may be employed again and again after filtering while warm through cotton wool and mixing with more solution of copper hydroxide, adding fresh phenylhydrazine when necessary to compensate for the dilution. If required for future use, the liquid must be kept in a stoppered bottle carefully protected from the air, as free oxygen is very readily absorbed by it and the phenylhydrazine thereby destroyed.

The mirrors obtained by this method are very beautiful, for they show the pleasing red colour of copper and are as perfect in reflecting surface and as lustrous as the similar mirrors obtained by the deposition of silver.

To carry out the operation successfully, it is essential to cleanse very thoroughly the surface of the glass; this is best done by well rubbing in turn

with a strong solution of soap, with strong nitric acid, and with strong caustic potash, using a pad of cotton wool soaked in these liquids, and washing well between the successive operations.

Surfaces of blown glass are more readily coated with copper than polished surfaces. In any case old glass should not be used, at least without the surface being carefully repolished.

Ammonia in excess hinders the deposition of copper, as it does that of silver, while caustic alkali accelerates it.

It is interesting to note that the copper is in the monvalent or cuprous state, in which it is analogous to silver, when it shows a similar tendency to be deposited in a metallic film upon glass.

Little is known as to the reasons why, when metallic oxides are reduced in aqueous solutions, the metals under certain conditions are deposited upon glass in a thin, reflecting lamina, while under others, apparently equally favourable to such deposition, they separate in a spongy or flocculent state. Vogel* concludes from his experiments with silver oxide that when complete reduction takes place in one stage, a mirror or crystalline deposit is obtained, whilst granular or finely divided silver is produced in two stages, a lower insoluble oxide separating as the primary product of the reduction and being afterwards itself further reduced.

The behaviour of copper oxide on reduction makes it, however, very improbable that the various stages of the process affect the result.

For the production of a mirror it appears rather to be essential that the compound undergoing reduction shall be in solution and that its concentration shall be small, that the liquid in which it takes place shall be alkaline, and that action shall be more rapid at the surface of the glass than elsewhere.

It is certain that the nature of the surface on which the metal is deposited plays an important part in the process, since both silver and copper are deposited much better upon blown than upon polished glass and upon surfaces which have not for long been exposed to the action of the air or of water.

It seems probable that the glass surface itself acts as a catalyser and locally accelerates the action.

Oberbeck, some years ago,† measured the electric resistances of a number of silver films deposited upon glass from aqueous solution.

He made the interesting discovery that such resistances, although very large immediately after the metal had been deposited, continually diminished with time, and although a minimum was not reached in two years, ultimately approximated to the resistances which would have been shown by films of

* 'Journ. für praktische Chemie,' 1862, vol. 86, p. 321.

† 'Ann. der Physik und Chemie,' 1892, p. 282.

ordinary silver of corresponding thickness and size. The films during this change of resistance altered neither in reflecting power nor in appearance when viewed by transmitted light.

As reflecting silver films of very different thickness and initial resistance and produced under very different conditions all showed this great increase in conductivity, Oberbeck concluded that when silver is first deposited from aqueous solution in the form of a mirror, it is in a different molecular condition from ordinary silver, but that in time its state approaches that of the latter more and more.

The Electric Discharge in Monatomic Gases.

By FREDERICK SODDY, M.A., Lecturer in Physical Chemistry in the University of Glasgow, and THOMAS D. MACKENZIE, B.Sc., Carnegie Research Scholar.

(Communicated by Professor J. Larmor, Sec. R.S. Received October 8,—
Read November 7, 1907.)

1. Scope of the Enquiry.

In a recent paper* one of us has described the use of metallic calcium at high temperature for the production of high vacua, and in spectroscopic work as a very perfect chemical absorbent of all except the chemically inert gases. It was shown that helium and argon purified by calcium from traces of common gases or vapours, with which they are in practice invariably contaminated during manipulation, showed a great disinclination to conduct the discharge. In ordinary spectrum-tubes, helium offered a resistance equivalent to an alternative spark-gap of an inch in air, at a pressure of 0.05 mm., and argon at 0.02 mm. of mercury. This behaviour of the monatomic gases, together with the closely-allied phenomenon shown by spectrum-tubes filled with these gases of becoming non-conducting, or "running out," under the action of the discharge, have now been investigated in detail. A great number of experiments have been performed and a short summary will be given in the present paper.

The main object was to settle whether electric conduction in the monatomic gases is essentially different from that in other gases. The first results raised at least a presumption that perfectly pure helium might

* 'Roy. Soc. Proc.,' 1907, A, vol. 78, p. 429.

be unable to conduct the discharge at all, so that the running out of spectrum-tubes might be due to the absorption of the impurities only by the electrodes and not by the absorption of the inert gas itself. This view, however, proved to be untenable.

The absorption of the monatomic gases during the discharge occurs rapidly and continuously under suitable conditions, and the nature of this action is now fairly clear. But, on the other hand, helium which has been subjected to the prolonged action of the discharge between aluminium electrodes, after initial purification with calcium, exhibits to an altogether extraordinary degree the peculiarity before noticed. In an ordinary spectrum-tube such helium offers a resistance equivalent to that of an inch spark-gap at a pressure of over half a millimetre of mercury, and the discharge is accompanied by all the well-known characteristics—intense fluorescence of the tube, production of cathode rays, and the incipient production of X-rays—which are usually supposed to be indicative of a high vacuum. But at higher pressures this very pure helium conducts the discharge in the same way as other gases. Our results leave no doubt that the difference between helium and other gases is one of degree only, and that the monatomic gases are relatively electrically as well as chemically inert. It will be shown that the remarkable behaviour of helium in the region of low pressure is intimately bound up with the equally remarkable behaviour of the gas in the region of atmospheric pressure, when, as Ramsay and Collie* have shown, it conducts the discharge so much more easily than any other gas. A spectrum-tube filled with helium at atmospheric pressure conducts the current from a small induction coil with ease. It is only necessary to regard the helium molecule at all pressures as only about one-fifth to one-tenth as effective electrically as a molecule of a common gas like hydrogen, in order to obtain a simple and consistent explanation of the behaviour of both high and low pressure helium to the discharge. In the course of the work it became necessary to examine the common gases also in order to be able to compare their behaviour with the monatomic gases. The result transpired that the electrical effects usually supposed to be indicative of a high vacuum occur in all gases at degrees of rarefaction which cannot with any accuracy be described as “high vacua.” Thus in the previous paper the behaviour of argon, which was found unable to conduct below 0.02 mm., was regarded as exceptional. In reality, it is similar at this pressure to the common gases, hydrogen and nitrogen, all of which, when pure, cease to conduct at about 0.04 mm. The pressure in an X-ray tube, filled with hydrogen and giving good X-rays, is above

* ‘Roy. Soc. Proc.’ 1896, vol. 59, p. 257.

0.01 mm. Some of the possible causes which may have contributed to the mistaken impression that the degree of rarefaction in a Crookes tube is of the order of a thousandth of a millimetre will be discussed in the paper.

During the investigation it transpired that the spectrum of one of the rare gases appeared in a set of new spectrum-tubes during preliminary preparation before any of the gas had been introduced; and it has been put beyond doubt that the aluminium electrodes of spectrum-tubes which have been used with either helium, neon or argon, retain, even after months' exposure to the air, sufficient of the gas in question to give its spectrum when remounted in a new glass tube into which none of the gas is introduced.

2. Absorption of Helium in Spectrum-tubes.

In our first series of experiments the running out of spectrum-tubes filled with helium was investigated. Six similar spectrum-tubes of about 28 c.c. volume were filled with helium purified by calcium to accurately known initial pressures, ranging from 1 to 32 mm. The tubes were constructed to stand a heavy current without breaking down. The cathode consisted of aluminium wire 4 mm. diameter, and the anode an aluminium disc 16 mm. diameter. A narrow side tube was sealed into the cathode chamber for the purpose of measuring subsequently the residual gas in the tube, and a tube drawn to a fine point, to be broken under mercury at the end of the experiment, was sealed to the anode chamber. These tubes were constructed in batches of a dozen at a time by a well-known London maker especially for the investigation, and none of them have been used in any other experiments.

Six tubes at a time were attached to the calcium furnace, an arrangement for admitting known quantities of helium, and a mercury pump, and very thoroughly freed from occluded gases by heating and passing a discharge heavy enough to fuse the electrodes. The remarkable fact must be chronicled that during this treatment, before any helium had been brought into the apparatus, the first batch of tubes developed the helium spectrum. In the two first experiments, each with six new tubes of the first dozen, the full helium spectrum was developed during the preliminary treatment. The second batch of a dozen, made at another time, did not show this behaviour. The phenomenon and its probable explanation are discussed under Section 9.

The practice adopted during this preliminary treatment was to keep the calcium at its absorbing temperature, and by a tap to regulate the flow of expelled gases into the calcium chamber, so as to keep the tube fluorescent without allowing the vacuum to rise to the non-conducting point. When the operation was complete and the calcium had absorbed the expelled gases,

helium was introduced, the fusion of the electrodes repeated, and the tubes again exhausted by the pump. This was necessary, as it is known* that electrodes freed sufficiently from occluded gases by ordinary running and heating tend to evolve a further supply when filled with the monatomic gases and run, owing to the much greater heating of the electrodes in the latter gases.

Helium in accurately known amount was then admitted to the calcium chamber and allowed to remain there until the spectrum became perfectly pure, when the tap to the spectrum-tube was opened and the first tube sealed off. The remaining five were then sealed off one by one, each after a further known quantity of helium had been admitted. The total volume of the apparatus had been found, so the initial pressure of helium in each tube could be calculated.

The six tubes were then run in series with a heavy current from a 10-inch coil worked with a mercury interrupter from the 250-V. mains. A rectifier was placed in the secondary circuit to keep the current as unidirectional as possible, but it is doubtful if this had any influence. The first four tubes showed a sharp line spectrum, but in the other two, owing to too high pressure, the spectrum was confused. A new clear faint line in the extreme red, about 7266, was noticed in the helium spectrum of the tubes filled at lower pressure.

The first three tubes ran out and became non-conducting without difficulty, and ultimately the fourth also, but the remaining two did not. All the first four tubes went through the same changes in appearance just before they became non-conducting. The glow changed from yellow to green, and the yellow line, at first by far the strongest, became weaker than the green. At this stage the cathode fluorescence extended a distance of 12 cm. to the extreme tip of the side gauge-tube. As soon as the discharge commenced to pass an alternative gap of 1 inch in parallel to the tube, the latter was cut out of circuit and the tip broken under previously heated mercury, with precautions against the admission of air. As the mercury entered, all the gas was compressed into the side gauge-tube and its volume marked by a diamond scratch. The table (p. 96) shows the details of the six tubes.

The current after the first 40 hours was considerably increased.

The pressures in the last column were obtained from the volume of the residual gas immediately after filling the tube with mercury. It will be seen that the helium is absorbed during the discharge until a residual pressure is reached nearly the same in each case and between 0.6 and 0.7 mm., independent of the initial pressure. This indicates that at this pressure the

* E. C. C. Baly, 'Phil. Trans.,' 1903, A, vol. 202, p. 185.

| | Initial pressure. | Fluorescence appeared. | Became non-conducting. | Residual pressure. |
|-----------|-------------------|--|------------------------|--------------------|
| | mm. | | | mm. |
| I | 1·1 | From start | After 25 mins. | 0·57 |
| II | 2·3 | After 10 mins. | After 70 mins. | 0·72 |
| III | 4·9 | After 50 mins. | After 7 hrs. 40 mins. | 0·62 |
| IV | 8·6 | After 60 hrs. 30 mins. | After 61 hrs. 20 mins. | 0·9 |
| V | 16·8 | } Did not appreciably change after over 100 hours' continuous running. | | |
| VI | 31·2 | | | |

helium ceases to conduct the discharge. But it was at once found that as soon as the mercury entered the tube it commenced to dissolve the mirror of aluminium deposited from the electrodes and to liberate the absorbed gas. In the first tube, after the volume of the residual gas had been measured, the mercury was sucked out and allowed to refill the tube, when the volume was found to have doubled. In the second tube the evolution of gas could be watched, and large bubbles made their appearance at the cathode film as the mercury was sucked out. The volume after refilling corresponded to a final pressure of 1·33 mm. In the third tube, after the mercury had been left in half an hour, the pressure was 3·43 mm., and after readmitting the mercury and allowing it to remain another four hours the pressure was 3·7 mm. In the fourth tube gas came out from both the anode and cathode mirrors, and the volume increased enormously, but the final measurement was unfortunately lost. The spectrum of the residual and liberated gas was always observed, to detect the entrance of air, but in every case the spectrum, except for mercury, was of absolutely pure helium.

These experiments clearly show the nature of the process when a helium tube is run to non-conductance. Contrary to what was given as the explanation in the last paper,* a real absorption of the helium takes place, and the greater part of the absorbed gas is very loosely retained and can be recovered from the aluminium mirror volatilised from the electrodes. On the other hand, non-conductance obtains in pure helium long before all the helium is absorbed, and the gas so treated refuses to conduct the current at a pressure when any other gas would be at about its maximum conductivity. As, however, the residual pressure was practically the same for all the four tubes, one of which had been run for over 60 hours, the experiments do not support the idea that pure helium by itself is a non-conductor. They favour the view that the constant residual pressure is the real limiting pressure for pure helium itself, above which it will conduct in the same way as any other gas.

* *Loc. cit.*, p. 448.

The experiments described are inconclusive in one respect. Owing to the unexpected ease with which the absorbed gas is liberated under the action of mercury, the large residual pressures observed might have been due at least in part to liberation of absorbed gas during the admission of the mercury. This did actually happen in the filling of Tube No. IV with mercury, and accounts for the somewhat high residual pressure observed. Before the cathode chamber had filled actual bubbles had been liberated from the aluminium film in the anode chamber and could be seen passing through the capillary with the entering mercury. It was, therefore, necessary to repeat the observations in a different manner to eliminate this uncertainty.

Before describing these it may be mentioned that a similar series of tubes to those used for helium were prepared with argon, but none of the tubes could be run out to non-conductance even after prolonged action of the discharge. During the greater part of the time the cathode in the tube filled at lowest pressure (1.3 mm.) was bright red-hot. Only this tube showed a clear spectrum. All the others filled to higher pressures had a confused spectrum. In filling the tubes we had the mistaken impression that argon was more easy to run out than helium. Argon spectrum-tubes certainly often run out more readily than those of helium, but this is due to the fact that the pressure in an argon tube is necessarily so much lower than in helium in order to get a clear spectrum. A good helium tube may be filled to 6 or 8 mm. without confusing the lines, but in argon the pressure should not be much over a millimetre. To get results with argon comparable with those for helium the tubes should have been filled to about one-tenth the pressures.

3. *The Pressure at which Pure Helium ceases to conduct.*

The advantage of experimenting with sealed tubes is that thereby the influence of contaminations derived from lubricants and mercury is eliminated. In the present series of experiments mercury vapour was present, and found not to exert any important influence; but lubricants were completely avoided in that part of the apparatus containing the helium while it was being run. The spectrum-tube was of the same pattern as before, but was kept connected throughout the experiment with a specially designed form of M'Leod gauge (fig. 1) by means of an unstricted tube. The graduated tube and the connecting tubes were 6 mm. in bore, and to avoid the latter being too long they were provided with glass valves closed by the rising mercury of the kind usually found on Töpler pumps. The gauge was worked without rubber tubing by varying the pressure on the mercury in the reservoir. By the special arrangement of tubes shown, the

spectrum-tube and gauge could be connected with or shut off from the rest of the apparatus by lowering or raising the mercury, so that the apparatus constituted a mercury tap as well as a gauge. Thus the vapour of lubricants was avoided, and during the running of the spectrum-tube the mercury sealed off the connection with the rest of the apparatus. With this

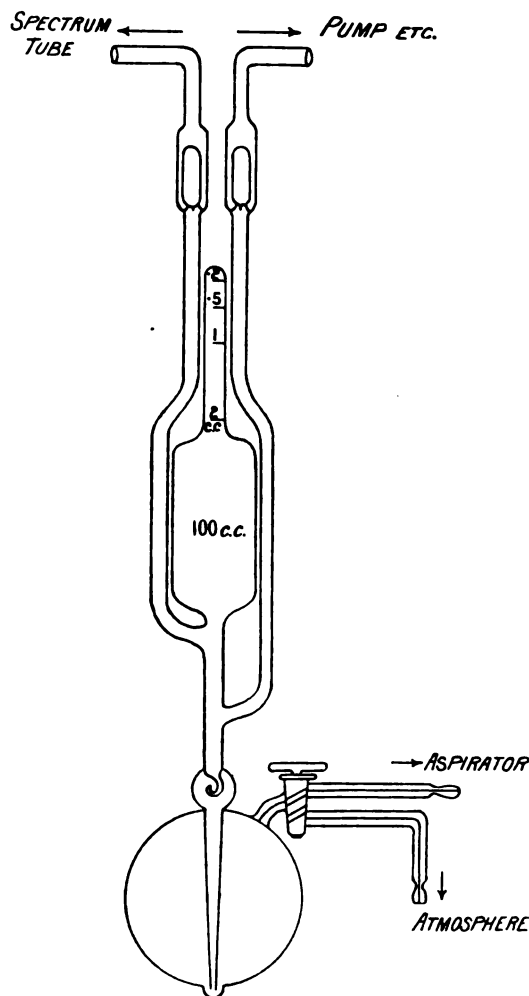


FIG. 1.

apparatus the earlier results were at once confirmed. If helium purified by calcium is admitted in successive small doses to the apparatus and run out till the discharge commences to pass an inch gap, the pressure at which non-conductance obtains reaches a maximum of 0.7 mm., and then the admission of more helium and further running to non-conductance always

reproduces this same pressure. In common gases the stage of non-conductance is usually reached very abruptly at a definite pressure, but in the monatomic gases a heavy current will partly spark across a given gap when a feebler current would pass entirely through the tube. The observations were, therefore, taken under as nearly comparable conditions as possible as regards the current flowing. Three stages were recognised in the experiments. In the first, sparks passed regularly at intervals of a few seconds; in the second, sparking was continuous, about half the current going through the gap; and in the third, only a very feeble current passed through the tube. The initial passage of a single spark or a few sparks at long irregular intervals across the gap was ignored. The pressure of 0.7 mm. corresponds to the first stage. If the pressure is measured after the second stage is reached, it is found to be about 0.55 mm. When the discharge is left to run for several hours until the third stage is reached and hardly any current passes through the tube, the pressure sinks to 0.35 mm., and does not further decrease however long the discharge is continued. Increasing the spark-gap to 2 inches only effects a very slight additional absorption of the gas, and external discharges take place over the glass, owing to the condenser effect of the aluminium mirror inside the tube, which involve the risk of puncturing the tube.

In this apparatus the pressure at which sparks from a small coil commenced to jump an inch gap was measured in helium which had been purified by calcium only and not subjected to the discharge. It was found to be 0.275 mm. This is over five times the pressure given in the last paper, and is due to a more thorough removal of gases from the electrodes prior to the experiment, and to the absence of vapour of lubricating grease. It is clear that running the tube exerts a further purification of the helium by the absorption of the last remaining impurities in the electrodes, and that an otherwise undetectable trace of impurity makes a very great difference on the pressure at which helium becomes non-conducting.

In helium purified by calcium and the prolonged action of the discharge, examined in a straight tube 30 mm. wide by 100 mm. long, with two 10 mm. discs of aluminium 42 mm. apart, continuous sparking across an inch gap occurred at a pressure of 0.39 mm. The total amount of gas admitted to this tube during the experiment was recorded. The tube was pumped out to 0.001 mm. On standing for 20 minutes the pressure had risen to 0.01, and after 18 hours to 0.034, due to the spontaneous liberation of helium in the cold. The tube was then heated, and the pressure rose to 0.36 mm. It was pumped out to 0.001, and reheated more strongly, when the pressure of the gas liberated was 0.5 mm. It was

calculated that at least 98 per cent. of the absorbed gas was re-evolved through heating. As at this temperature none of the gas which causes the Campbell Swinton effect (compare Section 10) is liberated, it follows that only a very small fraction of the absorbed gas is driven into the glass itself.

Experiments were made to see if helium is absorbed during simple volatilisation of aluminium and magnesium by heating these metals in a furnace similar to that employed for heating calcium. No absorption occurred. This suggests that the absorption in the case of helium is electrical or mechanical rather than chemical. The gas molecules moving under the electric force with great velocity resemble the α -particles, and are able, as Campbell Swinton's results indicate, to penetrate the surface of the glass wall to a very slight extent and remain embedded. If, however, the glass is covered with a mirror of aluminium, most of the gas is stopped there and does not reach the glass.

An arrangement was devised to compress helium after it had been purified by calcium and run till non-conducting in a spectrum-tube without thereby contaminating it. A second volume of about 100 c.c., capable of being filled with or emptied of mercury in the same way as the M'Leod gauge, was attached to the apparatus. The whole apparatus was first filled with helium and run to non-conductance, and mercury was then admitted to compress the helium, and the spark-gap measured. It was found that the gas behaved quite normally. Increasing the pressure lowered the spark-gap, and on expanding the original spark-gap was regained. The helium, owing to the larger volume of the apparatus, was not quite so pure as before, and the pressure in one experiment with the sparks passing an inch gap was 0.43 mm. At 0.68 mm. the gap was 12 mm., and at 1.64 mm. the gap was 3 mm. An attempt was made to get an approximate value in volts for the various spark-gaps by means of current from a large Wimshurst machine and a Kelvin electrostatic voltmeter. The gap of an inch or 25 mm. corresponded to 16,800 V., of 20 mm. to 12,500, of 10 mm. to 10,400, of 5 mm. to 7900, and of 2 mm. to 5100.

4. *Behaviour of Neon and Argon.*

The results obtained with neon and argon were quite analogous to those recorded for helium. With neon the first stage of non-conductance with an inch gap occurred at a pressure of 0.18 mm., the second at 0.10 mm. and the last at 0.07 mm. With argon a great many observations were made and the three pressures were 0.055 mm., 0.05 mm., and 0.04 mm. In one experiment with the latter gas the initial pressure in the tube was 0.27, and

it took four hours' running before the tube became non-conducting. During this time the pressure steadily decreased until the values given above were reached. Increasing the gap to 2 inches only effected a slight reduction of pressure to 0.037 mm. In an experiment with neon which had been run to the last stage and left, the pressure rose during the night from 0.075 to 0.09, and on heating the tube next morning a pressure of 0.4 mm. developed. Only 30 seconds' running sufficed to reduce this to 0.2 mm., when sparks commenced to jump the gap.

5. *Behaviour of Hydrogen, Nitrogen, and Carbon Dioxide.*

Similar experiments on the pressure at which non-conductance obtained were performed with the gases hydrogen, nitrogen, and carbon dioxide. With these the non-conducting point was very well defined. Thus with hydrogen practically no current went through the tube at a pressure of 0.04 mm. for a spectrum-tube, and 0.03 mm. for a wide tube of the kind described (p. 99). It was found that pure hydrogen, derived from palladium hydride, behaved in the same way as the gas introduced into the apparatus by heating, with a spirit flame, the palladium wire of a regulator such as X-ray bulbs are now commonly provided with for lowering the vacuum. Cathode fluorescence commences in hydrogen in a spectrum-tube at 0.1 mm., the gap was 5 mm. at 0.07 mm., and 10 mm. at 0.06 mm. In nitrogen non-conductance is reached at about 0.035 mm., and in carbon dioxide at about 0.02 mm., both for an inch gap. At a pressure at which a hydrogen tube would give an inch gap a carbon dioxide tube would give only a millimetre gap.

[Special experiments were performed with pure nitrogen to ascertain whether, after prolonged running, the pressure at which non-conductance set in was raised as in the case of helium, but with negative result. In a tube in which repeated additions of nitrogen were absorbed by the electrodes under the discharge, the pressure at which non-conductance occurred with an inch gap was the same at the end of the experiment as at the beginning with nitrogen which had not been run.—*October 21.*]

The gas generated from the electrodes and walls of a new spectrum-tube during running behaved, as its spectrum indicates, like a mixture of hydrogen and carbon dioxide and with an inch gap is non-conducting at 0.03 mm. It is remarkable how abruptly conducting power ceases when the pressure falls lower than 0.04 to 0.02 in common gases. The application of powerful coils may cause a discharge below these pressures, but only by first lowering the vacuum. The facilitation of the discharge by the use of electrodes of the alkali metals or calcium is analogous.

The action of these metals is probably to supply hydrogen sufficient to conduct the discharge. The evolution of hydrogen from calcium during heating formed the subject of frequent reference in the last paper. In operating the calcium furnace enough hydrogen is always evolved on heating a fresh piece of calcium to make the vacuum a far better conductor of heat than air at atmospheric pressure. Probably hydrogen-free calcium has never yet been prepared.

There are probably many other reasons, more or less well recognised, that account for the impression that the degree of rarefaction in a vacuum incapable of conducting the discharge is extreme. Apparatus to be exhausted is usually made with a constricted orifice where it is to be sealed off. The free path of the gas becomes comparable with the diameter of this constriction at about 0.1 mm., or higher in heavy gases and vapours. Below this pressure there is properly speaking but slight difference of pressure between the two sides of the orifice, using the word *pressure* in a hydrostatic sense, even though on one side a perfect vacuum is maintained. Diffusion alone, not flow, operates to equalise the concentration of the gas on the two sides, and therefore gauge readings of pressure in apparatus connected to the gauge with a narrow orifice are not strictly pressure readings at all. A more important error, probably, of the readings is the usually invariable presence of vapour which a compression gauge will not detect and a pump will not remove. In the present measurements constrictions were avoided and vapours removed by the action of calcium, and these two facts probably account for the pressures at which non-conductance obtains being comparatively high. It is doubtful whether the lower pressure recorded in the case of carbon dioxide is real or due to the property of carbon dioxide of condensing on glass surfaces, vitiating the gauge readings.

6. *Behaviour of Mercury Vapour.*

In the first series of experiments the mercury was contained in an H-tube provided with two electrodes, and was connected to a shortened fall-tube, which, when the mercury was boiled out, acted as a Sprengel pump worked with the condensed mercury. After the apparatus had been exhausted as completely as possible by the mercury pump, the mercury in the tube was rapidly boiled and the exhaustion continued by means of the condensed globules of mercury falling through the fall-tube. Owing to the liability of the glass to crack during prolonged heating the method was abandoned. But with this apparatus the cathode fluorescence of the discharge was not observed when the temperature of the mercury was above 90°, and the tube was non-conducting to an inch gap below 60°.

In the next experiments the apparatus was exhausted by means of calcium, the mercury being boiled vigorously, and a heavy discharge being passed through the tube during the operation. After this treatment the mercury remained non-conducting, and fluorescence was observed at much higher temperatures than if the calcium treatment had not been adopted. The cathode fluorescence was observed up to temperatures of about 110° , which corresponds to a pressure of 0.5 mm. The spark-gap was 10 mm. at a temperature corresponding to a pressure of about 0.15 mm., while below 0.1 mm. the mercury vapour conducted with difficulty. Hence mercury vapour resembles the monatomic gases both in the effect of impurities and the high pressure at which it remains non-conducting.

7. *Pressure in an X-ray Tube filled with Helium or Hydrogen.*

In order still further to test the view that helium conducts the discharge normally except for the higher pressure at which the various phenomena of the discharge make their appearance, an X-ray bulb of 8 cm. diameter was attached to the gauge in addition to the spectrum-tube, and the whole apparatus thoroughly freed from gas. Helium was admitted and run in the spectrum-tube till the discharge passed an inch gap at a pressure of 0.41 mm. The mercury in the gauge was then momentarily lowered, and small successive quantities of the helium removed by the pump, and the appearance of the X-ray tube observed. The hemispherical area of fluorescence accompanied by the production of X-rays just able to penetrate the glass was observed at a pressure of 0.31. At 0.25 mm. rays capable of penetrating 0.2 mm. of aluminium escaped the tube and the spark-gap was 1.5 mm. At 0.21 the spark-gap was 17 mm. and the bones of the hand could be well seen. At 0.15 mm. the spark-gap was 22 mm. and the flesh of the hand was quite transparent to the rays.

It must be pointed out in this experiment that the helium, though pure at the start, must have become contaminated as the pressure was reduced, owing to vapour from the rest of the apparatus diffusing back during the exhaustion, and to gas generated from the electrodes. For this reason the pressures corresponding to the longer spark-gaps are probably too low, and as the exhaustion proceeded, approached more and more closely to the values for a common gas like hydrogen. But, throughout, the appearance of the tube, but for the greenish glow at the commencement, was quite normal.

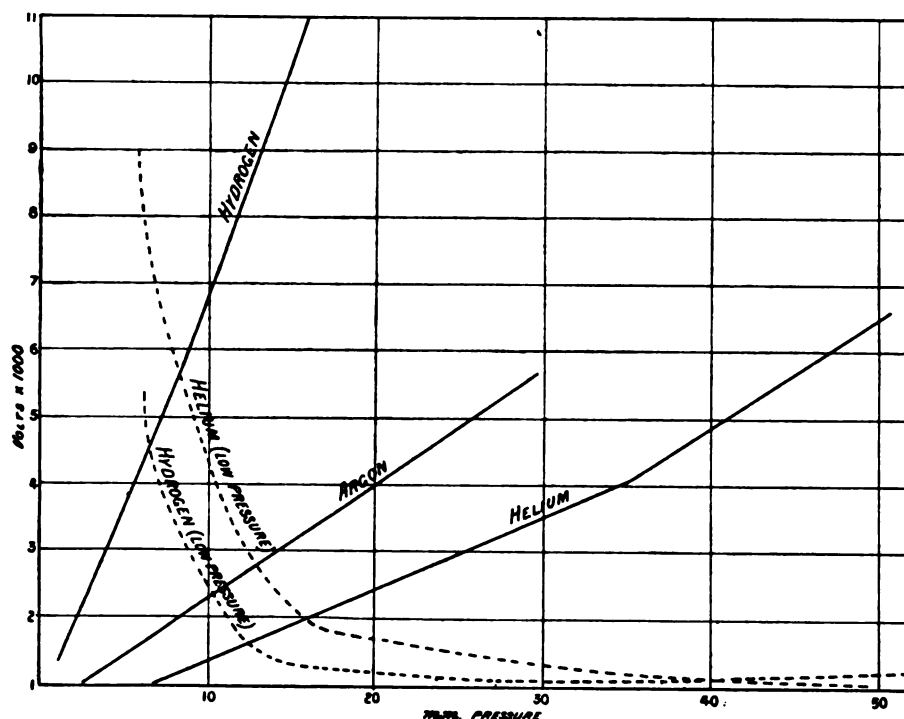
In the same X-ray tube, hydrogen derived from a palladium regulator gave the following values:—Fluorescence was plain at 0.13 mm., the gap was 10 mm. at 0.1, 20 mm. at 0.08, 30 mm. at 0.05, 40 mm. at 0.035, and 115 mm. at 0.02.

An X-ray bulb of the usual simple "bianodal" form and size, 13 cm. diameter, was attached to the gauge and exhausted entirely with the mercury pump in the ordinary way, the tube being heated in an oven and the discharge kept passing after the fluorescent stage had been attained. This operation took all day, whereas with calcium it could have been done easily within the hour. After cooling, the tube was run, and the pressures corresponding to different spark-gaps measured. The pressure varied from 0.008 mm. to 0.005 mm. with a gap from 4 cm. to 9 cm. The tube was then pumped as empty as possible, and subjected to the action of calcium to remove vapours. Hydrogen was then introduced through a palladium regulator. Now it was found that the pressures for corresponding spark-gaps were higher, and ranged from 0.045 with a spark-gap of 2 cm. to 0.012 with a spark-gap of 9 cm. It is probable that this difference is due to the absence of condensable vapours in the second case, and that in no case the real pressure in an X-ray tube is below the hundredth of a millimetre.

8. *The Relation of Potential to Pressure at High Pressures.*

On the view put forward to explain the high pressure at which helium becomes non-conducting, a space filled with a certain number of helium molecules conducts the discharge similarly in every way to the same space filled with about one-tenth to one-fifth the number of molecules of a common gas like hydrogen. This point of view at once brings into line the behaviour of helium at atmospheric pressure. At this pressure helium conducts the discharge in a similar manner to hydrogen at a pressure of several centimetres—that is to say, the discharge passes through helium at atmospheric pressure as a ribbon or flickering line of light. In order to investigate this point more closely, the curves connecting pressure and voltage in hydrogen and helium were compared in a very long wide tube by the aid of an 8-plate Wimshurst machine and a Kelvin electrostatic voltmeter. The current was kept constant, by regulating the speed of the machine, at about 0.3 milliampère. The voltage in hydrogen remained at a minimum of about 1100 V. from 0.62 to 0.3 mm., rising rapidly above and very suddenly below these limits. In helium the minimum potential was below 1000 V., the minimum range of the instrument, at from 6 to 0.54 mm. The tube was 70 cm. long, 25 mm. diameter, with two aluminium discs 15 mm. diameter, 64 cm. apart. The helium employed was spectroscopically quite pure at the commencement of the experiment, having been fractionated by charcoal cooled in liquid air, but no special effort was made to remove the unavoidable contaminations from taps, elec-

trodes, etc., introduced during the experiment. At 60 mm. the potential in helium was 7750 V., and in hydrogen this same potential was reached at 12 mm. In hydrogen at 30 mm. the potential was about 16,000 V., while in helium at the same pressure the potential was 3400 V. The smoothed curves are shown in the figure.



In the curves drawn in dotted lines the scale of the pressure axis is increased 100 times, so that these curves represent the relation of voltage with pressure up to 0.5 mm. In specially purified helium the curve would, of course, be very considerably displaced to the right.

The curve for argon at high pressure is also included in the figure, and it will be seen to approach helium more nearly than hydrogen. The fact that argon becomes non-conducting with an inch spark-gap at the same pressure as hydrogen does not truly represent the relation between the two gases, for at higher pressures up to the pressure of maximum conductivity, argon, like helium, conducts less readily than hydrogen, while in the region of high pressure it, like helium, conducts far more easily. The monatomic gases in general appear to be what has been termed electrically inert, and if the effectiveness of a molecule in allowing or resisting the passage of a discharge

is to be associated with the number of relatively free electrons it contains, the monatomic gases appear from their electrical, as well as from their chemical, inertness to be relatively deficient in easily displaceable electrons. But this point of view carries with it the corollary, since even in the purest state the monatomic gases are undoubtedly capable of conducting and becoming ionised, that their chemical inertness is relative rather than absolute. This was the view taken, we believe, by Dr. Larmor in connection with the previous paper.

Possibly the results described may be connected with the observations of Strutt,* who found the spark potential in helium and nitrogen greatly affected by minute traces of impurity, and of Warburg,† who found the cathode-fall in gases greatly affected by moisture and other impurities. But even if impurities exert a specific "catalytic" effect on the electrical properties of the gas with which they are mixed, apart from the effect proper to their partial pressure, it does not affect the conclusion that the monatomic gases are relatively electrically inert.

We wish to express our indebtedness to the Carnegie Trust for some of the apparatus used in the measurements given in this section.

9. *Retention of the Rare Gases by Aluminium Electrodes.*

In Section 2 it was recorded that a batch of new spectrum-tubes developed the helium spectrum during preparation, and the matter appeared to call for fuller examination. The conditions under which the spectrum-tubes were prepared were novel, in that the occluded gas was not pumped out, but absorbed chemically within the apparatus. Since six tubes with exceptionally heavy electrodes were treated at once, the conditions were very favourable for the detection of a minute trace of an inert gas produced by the discharge or evolved from the electrodes which otherwise would have been certainly overlooked. At first it was thought that the results might be connected with those of v. Hirsch,‡ who observed the continuous formation of a gas during the cathode-ray discharge, independently of the nature of the gas initially present, with properties which pointed to a possible molecular weight of 4. But Dr. von Hirsch about this time came and re-examined his gas in this laboratory by means of the calcium apparatus, and found it was certainly not helium.

A quantity of new aluminium wire and discs of the same kind as employed in the spectrum-tubes was procured from the maker of the tubes. This was heated to a very high temperature in a furnace similar to those employed for

* 'Phil. Trans.,' 1900, A, vol. 193, p. 377.

† 'Wied. Ann.,' 1890, vol. 40, p. 1.

‡ 'Phys. Zeit.,' 1907, vol. 8, p. 461.

calcium, but it failed to give the least indication of helium. Other spectrum-tubes at a later date from the same maker also did not give the least trace of helium when examined under conditions identical to those described.

The most probable explanation appeared to be that some of the electrodes in the first batch of tubes, probably the disc anodes, for the cathodes were almost certainly new, must have been old and used in previous experiments with helium before they came into our hands, and that such electrodes must be capable of retaining sufficient gas to show a spectrum when remounted in new tubes.

At the close of the investigation the second point was specifically examined. The electrodes of the tubes used in the experiments of Sections 3 and 4 were chosen for the test. The neon tube was first tried. It had been cut down five months before and since left open to the air. The cathode was first mounted in a new spectrum-tube with a new similar electrode fresh cut from a length of new aluminium wire of the same size and quality. It was attached to a calcium furnace through a tap and during the running the flow of gas was regulated to keep the tube fluorescent. As the spectrum cleared the neon yellow D_2 (5852.6) showed clear and distinct in the sodium, hydrogen, and mercury spectrum, its position being exactly fixed with reference to the two sodium lines. The tube was cut down and the disc anode of the old tube inserted in place of the new electrode, and then the tube was re-examined as before. Again D_2 was seen, but much brighter than before. After the calcium furnace had cooled, it was filled with mercury and the contained gas compressed about 15 times into a second spectrum-tube. Now the latter showed unmistakably to the eye the characteristic orange glow of neon, and the spectrum showed all the chief red and orange lines together with the helium line D_3 faint, and the lines of hydrogen and mercury. The original neon, which had been prepared by Mr. Berry by Dewar's fractionation method, showed the helium D_3 in about the same relative intensity. It can only probably be removed from the spectrum by fractionating the gas with liquid hydrogen. Contrary to the statement in Travers' "Experimental Study of Gases" (p. 312), the neon green line (5016) was not visible.

The helium tube was then examined. It had been cut down five months previously, but in this case had been sealed up, unexhausted, to exclude moisture. Both electrodes were sealed in a new spectrum-tube. The helium yellow D_3 was observed almost immediately after the commencement of running, and later the helium red (6677) faintly. From previous experience, the quantity of helium present could be accurately estimated. Its partial pressure was about 0.01 mm., and as the volume of the apparatus was about 200 c.c., the total quantity was about 3 cubic millimetres, measured at atmospheric pressure

This quantity would have given the whole spectrum brilliantly if the apparatus had been filled with mercury, but the result was certain without this being done.

The argon tube, like the neon tube, had been left open to the air for five months. The anode only was sealed into a new tube with a new electrode. It gave, on running, clear but faint argon lines in the blue region of the spectrum, and on compressing the gas at the end of the experiment the blue argon spectrum was clear.

[About a year previously, before any neon had been used in the laboratory, a number of old spectrum-tubes had been broken up and the electrodes recovered. These had since remained in an open dish exposed to air. A dozen of these electrodes, selected at random, were heated in a vacuum furnace to the melting point of aluminium, and the gases evolved absorbed by calcium in a second vacuum furnace. The helium yellow line, D_3 , was seen clear but faint. On compressing the gas about 14 times by admitting mercury, the prominent red and green lines of the spectrum were also seen. The quantity of helium was estimated to be about a fifth of a cubic millimetre.—October 21.]

These experiments, therefore, prove that aluminium electrodes tenaciously retain traces of argon, neon, and helium after they have been used in connection with these gases, and indicate that the explanation advanced for the extraordinary appearance of helium in the first batch of spectrum-tubes is probably correct and sufficient.

10. *The Campbell Swinton Effect.*

The glass parts of the spectrum-tubes, of which the electrodes had been used in the experiments described in last section, were examined for the effect described by Campbell Swinton,* who showed that if the glass of a vacuum-tube used with hydrogen or helium is fused in a flame it becomes clouded and under the microscope is seen to be permeated to some depth from the inside surface with a multitude of minute spherical bubbles. All three of our tubes showed this effect with the most remarkable clearness, but the argon tube was by far the best. Indeed, when the glass of this tube was fused it appeared to boil, and the bubbles could be seen and heard bursting. If the heating was stopped sooner the glass surface at first sight appears completely devitrified, but under a very small magnifying power the effect could be seen to be due to bubbles which were quite large where the glass had been most strongly heated. In the helium and neon tubes, and also the argon tube, the cathode chamber showed this effect everywhere where particles travelling at right angles to the surface of the wire cathode could reach the glass, but no effect whatever appeared behind the

* 'Roy. Soc. Proc.,' 1907, A, vol. 79, p. 134.

plane cutting the wire cathode at right angles drawn through the end of the glass tube in which the cathode was sheathed. The anode chamber of the helium and neon tubes showed a well-marked line of bubbles corresponding to the edge only of the anode disc, absent on the side where the side tube had been attached. In the argon tube this was absent, but the small part of the anode chamber immediately bordering on the capillary was strongly affected.

[The fact that the argon tubes showed the effect so prominently raised a doubt whether Campbell Swinton's explanation, that the bubbles are caused by the discharge gases being driven into the glass and remaining embedded below the surface, could be correct. Some of the glass from the argon tube was heated in an iron tube in a vacuum furnace, and the gases absorbed in a second furnace by calcium. The temperature, subsequently determined by a platinum and platinum-iridium couple, was in the neighbourhood of 1300°C . The glass frothed copiously, and was largely blown out of the iron tube. Argon, if present at all, could only have been but the merest trace as, although a faint argon spectrum was observed, it was not more than could be accounted for by a slight leak in the apparatus which interfered with the test. Certainly the main frothing of the glass was not due to embedded argon, and probably no argon was given off by the glass.

It was considered more satisfactory to try the glass of the neon and helium tubes in a similar way, as the appearance of these gases, if observed, is less equivocal than in the case of argon. No trace of neon was obtained from the glass of the neon tube which showed the Campbell Swinton effect strongly. With the glass of the helium tube the line D_3 was faintly visible. Some more of the glass was, therefore, first heated in an exhausted tube of Jena glass to a red heat to drive off gases condensed on the surface. The temperature was not high enough to develop bubbles, and the glass remained quite clear. This glass was then heated in a vacuum furnace as before to about 1300°C . No trace of helium was observed, even when the apparatus was filled with mercury.

These experiments show that the gas which causes the bubbles is not the discharge gas driven into the glass. The bubbles are in all probability a secondary effect, due to the chemical decomposition of the glass under the influence of local heating produced during the bombardment. There are probably in glass always sufficient undecomposed carbonates or sulphates to account for the effect, for porcelain, which is fired at a far higher temperature than glass, gives off a copious supply of gases consisting largely of carbon dioxide and hydrogen when heated in a vacuum above 1000°C . If the experiment is prolonged, several cubic centimetres of gas may be pumped off.—October 21.]

Note on the Sensibility of the Ear to the Direction of Explosive Sounds.

By A. MALLOCK, F.R.S.

(Received October 22,—Read November 21, 1907.)

Soon after the introduction of modern rifles, which give their projectiles a velocity much higher than that of sound, I noticed that when standing in a position in front of the gun and not far from the line of fire, the sound seemed to come, not from the firing point, but from some point considerably in advance of the gun. The natural explanation seemed to be that the sound thus heard was not that of the explosion itself, but was caused by the wave-surface, which is generated in the air by the projectile, moving at a velocity higher than sound. In 1898 I made some observations at the ranges at Broudown to see if the apparent directions agreed with this supposition. A large range like Broudown, however, at which many parties are firing at the same time, was not a very good place for such observations, but in the present year I have again made similar experiments under much more favourable circumstances. It is clear (if the source of the sound is due to the wave caused by the projectile) that the apparent direction of the sound will be the normal to the wave-surface, and that if the direction of this normal is known the velocity of the projectile, at the time that that particular portion of the wave-surface was generated which ultimately reaches the observer, can be calculated.

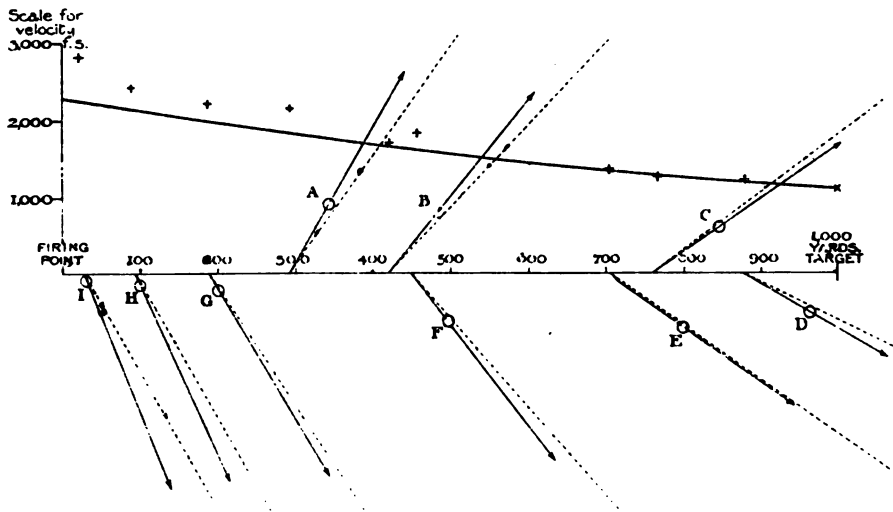
I now record these observations, not as giving a practical method of ascertaining the velocity of projectiles, but as showing that the ear can distinguish with considerable accuracy the direction of a sound which consists not of a train of waves, but, at most, of two waves only. The figure gives the plan of the range and the stations at which the observations were made.

The arrows through these points show the direction of the sound as judged by ear. Each arrow is the mean of eight observations which rarely differed among themselves by more than two or three degrees.

That portion of the wave-surface which passes the observer at any station was generated at the point where the apparent direction of the sound cuts the line of fire, and since the trace of the wave on the trajectory necessarily has the velocity of the projectile at the place where it was formed and moves along the normal with the ordinary velocity of sound, it is plain that at those points the velocity of the bullet is the velocity of sound \div the sine of the angle which the tangent to the wave-surface makes with the trajectory.

Sensibility of the Ear to the Direction of Explosive Sounds. 111

The spots, +, show the velocities thus computed, and the full curve gives the actual velocity, as determined by firing, at various ranges up to 1000 yards, into a ballistic pendulum.



The arrows show the apparent direction of the sound at the stations A B C . . .

The dotted lines are the normals to the wave-surface, calculated from the known velocity of the projectile.

The full curve is the velocity of the projectile, obtained from experiments with the ballistic pendulum.

The spots, +, are the velocities of the projectile, as deduced from the observed direction of the sound.

The method by which the observations of the direction of the sound were made rendered it almost impossible for any bias on the part of the observer to affect the result.

At each station a piece of paper fixed to a drawing board was placed on the ground and a line ruled on it was directed to the firing point. At each shot the observer determined in his own mind what point in the horizon the sound seemed to come from (this could be located by reference to some distant tree or other object), and a line was then drawn on the paper in that direction.

After all the observations had been completed a plan of the range was made from the 25-inch Ordnance Map and the positions of the observing stations were marked. The observed angles between the direction of the sound and the line joining the station with the firing point were then laid off, and thus the angles between the direction of the sound and the line of fire were found.

112 *Sensibility of the Ear to the Direction of Explosive Sounds.*

The agreement of the values of the velocities thus obtained with the true velocities shows the degree of accuracy with which the direction of the sound was estimated. In this case the difference between the true and observed directions was seldom more than a few degrees and was generally in one direction.

A sound which is caused by the detached waves, such as those which accompany a bullet, can scarcely be said to have a pitch, but the wave-length is certainly small compared with the distance between the ears, and is indeed comparable with the dimensions of the bullet itself. It would seem, therefore, that the ears can determine the direction of a sound, not only by difference of phase, but by the actual difference in the times at which a single pulse reaches them.

It may be mentioned that the difficulty in determining the apparent direction of the sound increased considerably as the observer approached the firing point, for there the noise of the actual explosion became comparable with that caused by the bullet. At a distance of 500 yards the noise of the explosion was inconsiderable and at 1000 yards almost inaudible.

Magnetic Declination at Kew Observatory, 1890—1900.

By C. CHREE, Sc.D., LL.D., F.R.S., Superintendent, Observatory Department,
National Physical Laboratory.

(Received November 2,—Read December 12, 1907.)

(From the National Physical Laboratory.)

(Abstract.)

The paper deals with the phenomena exhibited by the magnetic declination at Kew from 1890 to 1900. The magnetograph curves have been measured on every day of this period, whether disturbed or undisturbed, and the data from days of the different species are contrasted. Diurnal inequalities are got out for ordinary days, excluding those of large disturbance, and separately for the highly disturbed days, and the differences between these, and the points wherein they differ from the corresponding inequalities from *quiet* days, are investigated.

The disturbed days show a well-marked regular diurnal variation, which differs in many notable respects from that observed on ordinary days.

When the inequalities are analysed in Fourier series, it is found that the difference mainly centres in the 24-hour term, whose amplitude and phase seem both largely influenced by disturbance. The variation in the phenomena presented by disturbances throughout the year are investigated from several points of view.

The *absolute range* of the declination (absolute maximum less absolute minimum) was determined for every day of the 11 years, and special attention is given to the variation of this quantity throughout the year, and from year to year. With a view to throwing light on the theories of Arrhenius, Maunder and others, on the origin of magnetic storms, a minute comparison is made of the relationship between the absolute ranges and (Greenwich) sunspot areas throughout the 11 years. Whilst the results do not preclude the possibility that Arrhenius' theory may be true of a certain number of magnetic storms, they seem to indicate that it cannot be a complete explanation of the facts.

The paper aims at reaching results of a novel or critical character, and makes no attempt to chronicle the very bulky material, embracing over 100,000 actual curve readings, on which it is based.

The cost of the reductions has been partly defrayed by a grant obtained from the Government Grant Committee in 1904.

On the Frictional Resistances to the Flow of Air through a Pipe.

By JOHN H. GRINDLEY, D.Sc. (Vict.), and A. H. GIBSON, M.Sc. (Vict.).

(Communicated by Professor Horace Lamb, F.R.S. Received April 19,—Read May 23,—Received in revised form October 24, 1907.)

| | PAGE |
|---|------|
| § 1.—Introduction | 114 |
| § 2.—Description of the appliances | 115 |
| § 3.—The theory of the flow of a gas through a pipe and the deduction of general equations required in the research | 118 |
| § 4.—The determination of the essential dimensions of the experimental tube | 121 |
| § 5.—The method of conducting the experiments and the details of a typical experiment | 122 |
| § 6.—The results of the experiments..... | 125 |
| § 7.—The determination of the critical velocity for the flow of air in the tube | 130 |
| § 8.—The determination of the coefficient of viscosity and its variation with temperature..... | 130 |
| § 9.—The determination of the resistances to the passage of air in eddying motion through the tube, with a determination of the true equation of flow | 135 |

1. *Introduction.*

The research described in this paper was commenced by Dr. Grindley at the suggestion of Professor Osborne Reynolds in the Whitworth Engineering Laboratories, the Owens College, Manchester. Mr. Gibson continued the research after Dr. Grindley had left Manchester.

The experiments were commenced with the object of determining, on a larger experimental scale than usual, the coefficient of viscosity of air and other gases and the variation of this coefficient with temperature.

The present research, however, developed into a more complete investigation of the resistances to the passage of air through a pipe. The velocities of flow of the air through the pipe in the experiments by Dr. Grindley were for the most part above the critical velocity, the critical velocity being the velocity of flow below which the motion is steady or stream line and above which the motion becomes eddying or turbulent, the laws of resistance to the passage of the air being different in the two kinds of flow.

These experiments by Dr. Grindley indicated the value of the critical velocity of flow through the particular pipe used in the experiments, but the few experiments at velocities of flow below the critical were insufficient to

permit any deductions on viscosity to be made, and it was left to Mr. Gibson to make all the experiments at velocities of flow below the critical, from the results of which the coefficient of viscosity has been deduced in this paper.

The scope of the research may best be shown by the following summary of some of the more important deductions.

(1) The coefficient of viscosity, μ , of dry air at 0° C. is 0.0001702 in C.G.S. absolute units.

(2) The law of variation of μ with temperature has been determined between the temperature limits 0° C. and 100° C., and is found to be represented by an equation of the form

$$\mu = \frac{K\tau^{\frac{1}{2}}}{1 + C\tau^{-1}},$$

where K and C are constants, and τ is the absolute temperature.

(3) The absence of dependence of μ on the density of the air has again received experimental verification.

(4) The critical velocity for a small lead pipe—about 1/8 of an inch diameter—has been determined.

(5) In the turbulent motion of air through a pipe, the resistance has been found to be independent of the pressure of air in the pipe, and to be proportional to (velocity)ⁿ, where $n = 1.25$ for this pipe.

(6) The law of variation of this resistance with temperature has been determined.

2. Description of the Appliances.

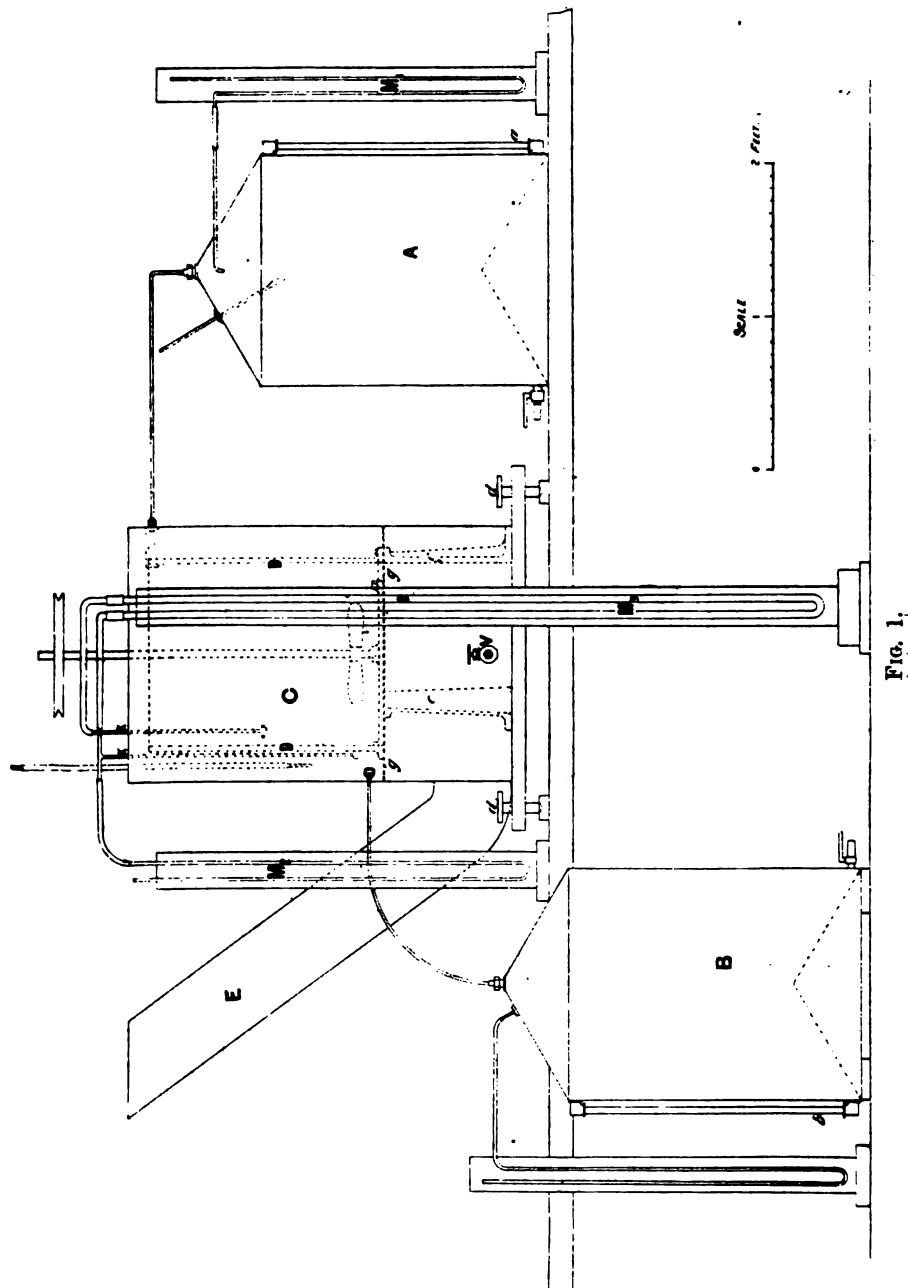
The general arrangement of the apparatus is shown in fig. 1. It consists of two gasholders A and B each of a little over 3 cubic feet capacity and connected by a length of lead tubing of roughly 1/8 of an inch internal diameter. Part of this length is to be used as the experimental tube, and at the ends of this, arrangements for measuring the pressures are provided.

The gasholder A contains air which can be forced through the experimental tube and into B by the simple expedients of admitting water into the lower part of A and emptying B of water contained by it at the beginning of each experiment.

These vessels A and B were calibrated so that the volume of air leaving or entering in any time interval could be obtained at once from the graduated gauges *aa* and *bb* by observing the heights of the columns of water in these tubes.

The length of tube between A and B is practically all wound on a central cylinder of brass D, the tube being wound at a constant small tension and fitting into a properly turned helical groove on the outer surface of the drum,

the groove being just wide enough to take the tube, and about $\frac{5}{32}$ of an inch deep, the pitch of the helix being one-third of an inch.



This cylinder D rested on three supports *c, c, c*, so as to occupy the upper central portion of a large circular vessel C of diameter 20 inches and height.

30 inches. The axis of the cylinder D was made vertical by means of the three levelling screws *dd* in the table supporting the vessel C. For making experiments at different temperatures, the vessel C was filled with water, which could be raised or lowered to any desired temperature by admitting steam through the valve V or by introducing ice into the lower part of C by the side chute E. A wire gauge *gg* for keeping the ice in the lower part of the vessel, a screw stirrer and a thermometer were also provided in vessel C.

The total length of lead tube inside the vessel C was about 190 feet, of which about 75 feet, or 20.1 coils, were used to change the temperature of the air which is flowing through the tube to that of the surrounding water before it passes into the experimental part, which consists of about 108 feet of tubing, or over 29 coils. From the end of the experimental tube a further 8 feet of tube passed the air into the gasholder B.

The pressures in A and B and at the ends of the experimental tube are required, and those for vessels A and B were obtained by two mercury manometer gauges, M_1 and M_2 . The pressures at the ends of the experimental tube required to be taken very accurately, and they were obtained in the following manner:—At each end of the experimental tube, the tube was raised out of its groove on cylinder D, as shown in fig. 2, G and G being

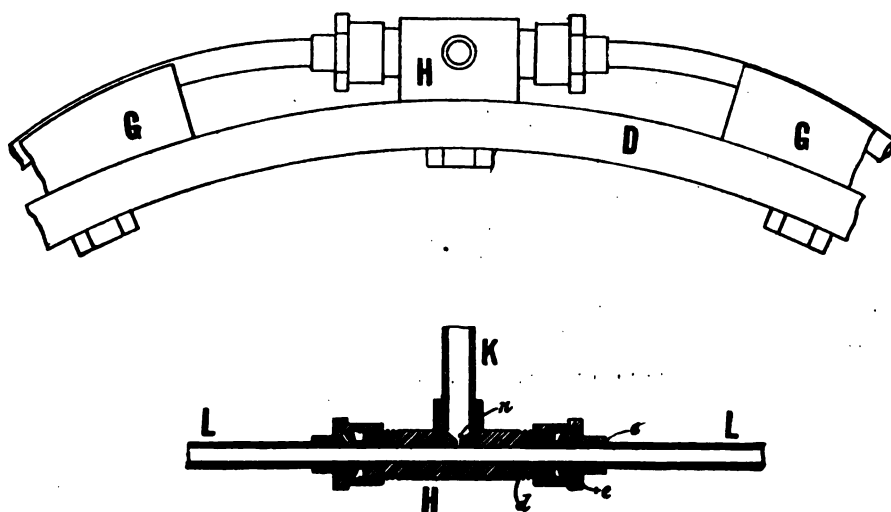


FIG. 2.

two brass grooved pieces fastened to the drum D. H is also a brass piece fastened to the drum D, but having a central hole of diameter equal to the mean internal diameter of the lead tube. From this passage the pressure of

the air is taken by means of the small hole n , leading to the vertical tube K (shown in fig. 1 and partly in fig. 2), which in turn communicates with the pressure gauges. As shown in fig. 2, the experimental tube LL enters the flanged nipple R, and is soldered to this at Q.

The pressures are read from the vertical pressure tubes KK as follows:—The low pressure end of the experimental tube is in communication with two gauges, one (a mercury gauge) giving the actual pressure at this point, while the second (a water gauge with inclined scale), M_3 , was also in communication with the high pressure end of the tube, and thus recorded the pressure difference along the experimental tube.

It is estimated that the limit of accuracy attainable with this pressure gauge was in the neighbourhood of 1 in 250, and in consequence the results of any experiment cannot claim any further degree of accuracy than about one-half of 1 per cent.

In all experiments carried out below the critical velocity, drying tubes were placed below the gasholder A and the experimental tube.

For much assistance in making the apparatus, the authors are indebted to Mr. T. Foster, of the Whitworth Engineering Laboratories at the Manchester University.

3. *Theoretical Considerations.*

When the velocity of flow of the air through the pipe is less than the critical velocity, the equation connecting the flux and the fall of pressure is easily deduced* from the definition of the coefficient of viscosity. It appears that if a is the inner radius of the pipe, l its length, and $p_0 - p_1$ the difference of the pressures at the ends of the experimental pipe, the coefficient of viscosity is given in absolute measure by

$$\mu = \frac{\pi a^4}{8l} \cdot \frac{p_0 - p_1}{w}, \quad (1)$$

where w is the volume of air flowing across any section of the pipe per second. In the experiments, w is taken as the quantity of air passing through the tube per second at the mean pressure $\frac{1}{2}(p_0 + p_1)$ of the air in the pipe.

When the velocities of flow are greater than the critical, the form of the equations of motion depends on the assumptions made in the estimation of the resistances. The usually accepted law for the resistance R_1 to the passage of a fluid moving with mean velocity u over a surface of area Δ is given in gravitational units by the equation

$$R_1 = \zeta \frac{D}{2g} \cdot u^2 \Delta, \quad (2)$$

* See Lamb, 'Hydrodynamics,' 3rd edit., p. 544.

where D is the weight per unit of volume of the fluid, and ζ is a coefficient usually termed the coefficient of friction.

The chief assumptions here made are that the resistance varies with the density of the fluid and with the square of its mean velocity. With compressible fluids, however, the laws of resistance represented by equation (2) have been assumed without adequate experimental basis. On integrating the equations of motion for the air in the pipe, assuming these laws of resistance, we are led to the following equation for the initial velocity u_0 of the air entering the experimental pipe :

$$u_0^2 = gR\tau(p_0^2 - p_1^2)/p_0^2 \left(\frac{\zeta l}{m} + \log_e \frac{p_0}{p_1} \right), * \quad (3)$$

where R is the constant in the characteristic equation for air $pv = R\tau$, p_0 and p_1 the pressures at the beginning and end of the experimental pipe, l the length of the tube, and m its hydraulic mean depth. If the difference of pressure $p_0 - p_1$ is relatively small, the term $\log_e p_0/p_1$ is usually neglected, and equation (3) written

$$u_0^2 = gmR\tau(p_0^2 - p_1^2)/\zeta lp_0^2. \quad (4)$$

This equation (4) is applied in this paper to the experimental results, but the values of ζ , calculated from the experimental numbers, showed such wide variations that it was thought advisable to test the assumptions embodied in (2) if possible.

If a general equation for the resistances R_1 to the motion of any gas over any surface of area Δ were constructed, it would include factors for possible variations of R_1 with the pressure, temperature, and the velocity of the gas, and with the shape, dimensions, and state of the tube's inner surface. Since the variation in density in any experiment at constant temperature has a corresponding pressure variation, we may assume for each experiment an equation for the resistance to motion in the form

$$R_1 = f\Delta p^r u^n, \quad (5)$$

where the coefficient f should be independent of the pressure p and velocity u of the gas, though it may vary (a) with the nature of the gas, (b) with the temperature, and (c) with the state of the tube's inner surface.

Equation (2) is a special case of (5) with

$$n = 2, \quad r = 1, \quad \text{and} \quad f = \frac{\zeta}{2gR\tau}, \quad (6)$$

since $D = p/R\tau$ in equation (2).

* See 'Encycl. Brit.,' art. "Hydraulics," vol. 15, p. 491.

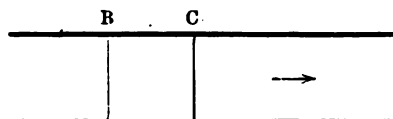
To form the equations of motion, using (5), let

S = perimeter of cross-section of tube ;

A = its uniform area ;

W = weight of gas passing any section of the tube per second ;

p = mean pressure across any cross-section B ;



$p + \delta p$ = mean pressure across any section C distant δx from B ;
and consider the forces on the mass of gas between B and C ; the principle of momentum would give at once, u being the mean steady velocity across the section of the tube,

$$-A\delta p = \frac{W}{g}\delta u + fSp^ru^n\delta x. \quad (7)$$

But $W = Au/v$, when v is the specific volume of the gas, hence $W = Ap/R\tau$, and since the temperature is constant during any experiment, we have $p^n = p_0^n u_0^n$, so that

$$W = p_0^n u_0^n A / R\tau. \quad (8)$$

By substitution in (7) and dividing throughout by Ap^ru^n we obtain in the limit

$$\frac{dp}{u^n p^r} + \frac{W}{Ag} \frac{du}{u^n p^r} + f \frac{S}{A} dx = 0. \quad (9)$$

But $u^n p^r = u_0^n p_0^n p^{r-n} = u_0^n p_0^n u^{n-r}$;

thus
$$\frac{p^{n-r} dp}{p_0^n u_0^n} + \frac{W}{Ag} \frac{u^{r-n} du}{p_0^r u_0^r} + f \frac{dx}{m} = 0,$$

where $m = A/S$ is the "hydraulic mean depth" of the pipe. Integrating, we get

$$\frac{p_0^{n-r+1} - p_1^{n-r+1}}{(n-r+1)p_0^n u_0^n} + \frac{W}{Ag} \frac{u_0^{r-n+1} - u_1^{r-n+1}}{(r-n+1)p_0^r u_0^r} - f \frac{l}{m} = 0. \quad (10)$$

It is usual to omit the middle term in this equation as being very small compared with the other two terms ; and as this is undoubtedly so in the present experiments, we may write

$$f/l/m = (p_0^{n-r+1} - p_1^{n-r+1}) / (n-r+1)p_0^n u_0^n. \quad (11)$$

If, now, we write w for the mean volume of gas passing through the tube per second at the mean pressure $\frac{1}{2}(p_0 + p_1)$ or p_m , we have $w = Au_m$, where u_m is the mean velocity in the tube or, as we shall here use it, the mean velocity

of the gas at the section of the tube where the pressure is p_m ; hence $p_0 u_0 = p_m u_m = p_m w/A$, and finally

$$f = \frac{mA^n}{l(n-r+1)} \cdot \frac{p_0^{n-r+1} - p_1^{n-r+1}}{p_m^n w^n}, \quad (12)$$

an equation resulting from the above hypotheses and deduced in the usual manner, connecting the coefficient of friction f with the flux through the pipe, to be compared with the experimental results. It is identical with the usual equation (4) if we write $n = 2$ and $r = 1$, and the reason for its deduction is to see whether these values of n and r are the most consistent with these experiments. How far the numbers obtained by applying this equation to the experimental results are influenced by the dimensions, etc., of the particular pipe used is not clearly known, and the method of deducing the equation itself is not free from objection, but as it is the usual method it has been adopted.

4. *Determination of the Essential Dimensions of the Appliances.*

Length of Experimental Tube.—The circumference of the coil on the drum was measured by wrapping thick drawing paper round the cylinder and correcting the outside diameter thus obtained for the tube radius to obtain the mean diameter of the coil. The number of coils was counted and the total lengths of coil between the pressure points were 108.8 feet in the coil used by Dr. Grindley and 108.2 feet in that used by Mr. Gibson.

Determination of the Internal Diameter of the Tube.—The method adopted was to take two short lengths (about 1 foot) from the beginning of the tube before winding and two similar lengths from the other end after winding the tube on the drum. From the mean external diameter and the weight of each length the mean internal diameter was deduced and found to be 0.1276 inch in the tube used by Dr. Grindley and 0.1248 inch for the second tube used by Mr. Gibson.

To check this method, after the experiments were concluded the second tube was flooded eight times with water, the volume of water occupying the tube being carefully measured in each case, and the diameter by this method was found to be 0.1246 inch at 62° F.

From these figures we obtain for a temperature of 62° F., for the first tube $\pi a^4/8l = \text{antilog } 12.4597$ and for the second tube $\pi a^4/8l = \text{antilog } 12.42105$.

At any other temperature the value of this factor, $\pi a^4/8l$, requires a correction for the temperature difference from 62° F.

To simplify calculation, equation (1) was put in the form

$$u = C(p_0 - p_1)^{1/n},$$

and the constant C determined so that the values of $p_0 - p_1$ in inches of mercury at 32° and w in cubic feet per second, as given directly by the experiments, could be inserted at once in the equation to give μ in foot-pound-weight-second units. Thus with the first tube $C = \text{antilog } 10.30876$ at 32° F. and with the second tube $C = \text{antilog } 10.27006$ at 32° , with an addition of 0.0000202 to the logarithm for each degree difference of temperature from 32° .

5. *Method of Conducting the Experiments.*

The first series of experiments, viz., those numbered 1 to 68, were made by Dr. Grindley and were carried out with the double purpose of finding the coefficient of viscosity of the air, and of determining the critical velocity for the tube by finding approximately the pressure difference at the two ends of the tube necessary to produce unsteady motion of the air. In the majority of these experiments, the results of which are plotted in fig. 3 and given in Table I, the velocities of flow were above the critical, and for the determination of the coefficient of viscosity they were of little use. They showed, however, the difference of pressure below which it was necessary to work in order that the velocity of flow should be below the critical, and, further, gave information on the resistance to flow at velocities above the critical. The experiments were therefore continued by Mr. Gibson, the majority of these being carried out at velocities well below the critical. Of this second series of experiments, the results of those above the critical velocity are shown in fig. 3 and in Table II, while the results of those below the critical point are given in Tables III, IV, V, and VI.

In every experiment, the procedure was as follows:—The coil and reservoirs having been levelled, the water bath was raised to the required temperature. This temperature being steady, after the expiration of about 15 minutes the regulating cocks on both air reservoirs were adjusted so as to give as nearly as possible the required pressure difference along the pipe. The temperature in the high-pressure air vessel was then noted until it became steady.

Having got all the temperatures and pressures, as well as the pressure difference between the two ends of the pipe (measured by the differential gauge) constant, three readings of the water level in each of the two air vessels were taken at intervals of 30 seconds. The temperatures of the air in vessel No. 1, and of the external air, as well as of the water bath, were then taken, and from this time to the end of the experiment the pressures in the two reservoirs and the pressure difference at the two ends of the tube were read at intervals of three minutes.

The temperatures of the external air, of the air in the high-pressure reservoir, and of the coil, were taken at intervals of nine minutes, being practically constant throughout the experiment. The relative and absolute pressures in the two reservoirs were regulated as necessary during the

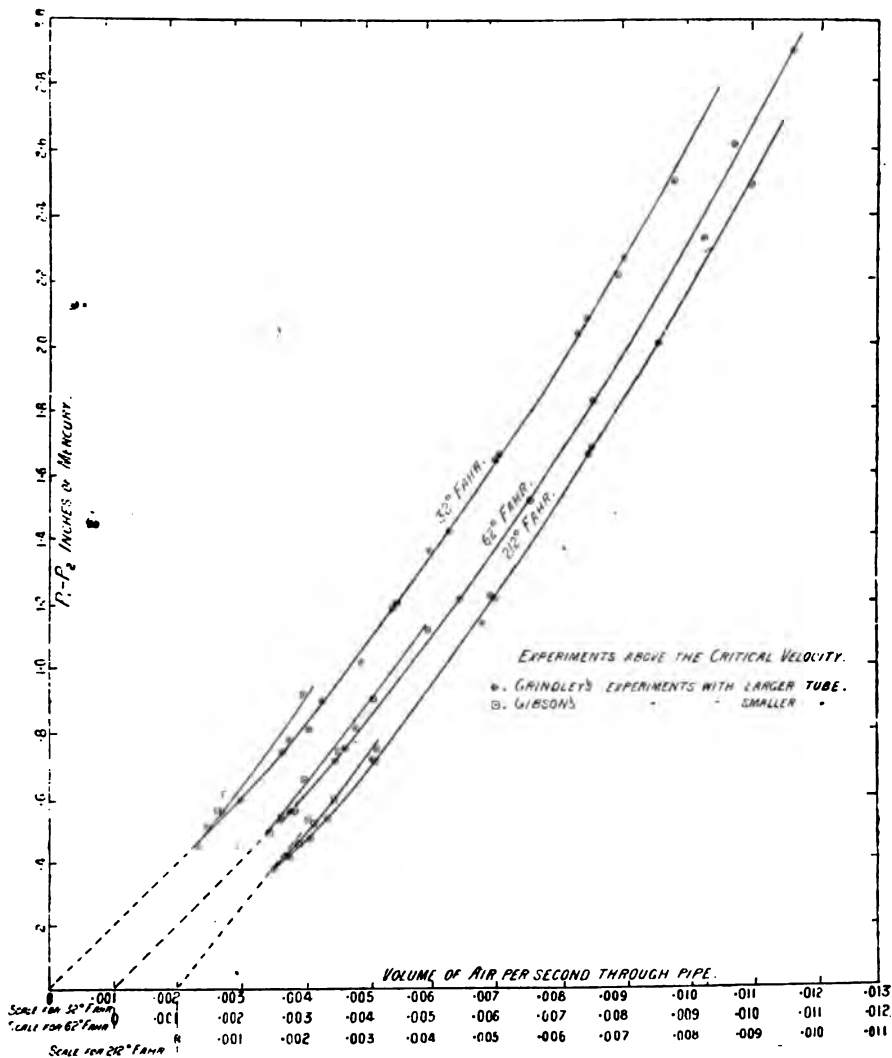


FIG. 3.

experiment by adjustment of the water inlet and outlet valves. In every case the experiment was terminated when the temperature in the high-pressure reservoir was identical with that at the start. Three readings of the water level in each of the air vessels were then taken at intervals

Experiment 172.—December 18, 1905.

| Time. | Pressures. | | | Temperatures. | | | | Volumes of water. | | | | | |
|---|---------------------------|----------------------------|---------------------|--|--------------|---------------------------|---------------|-------------------|------------------|------|-------|---|---|
| | Reservoir I (ins. Hg). | Reservoir II (ins. Hg). | P_1 (ins. Hg). | ($p_0 - p_1$) in inches of water multiplied by the gauge factor 1/0.869. | Air. ° F. | Reser- voir I. ° F. | Coil. ° F. | Reservoir I. | Reservoir II. | | | | |
| 2.50 | 0.55-0.05 | 0.50 | 0.00-0.00 | 0.00-0.00 | 0.02 | 0.06-0.04 | 2.70+1.44 | 4.14 | 66.8 | 68.0 | 163.2 | $\begin{cases} 1.410 \\ 1.413 \\ 1.417 \end{cases}$ | $\begin{cases} 2.310 \\ 2.314 \\ 2.318 \end{cases}$ |
| 2.53 | 0.55-0.05 | 0.50 | 0.00-0.00 | 0.00-0.00 | 0.02 | 0.06-0.04 | 2.71+1.45 | 4.16 | | | | | |
| 2.56 | 0.55-0.05 | 0.50 | 0.00-0.00 | 0.00-0.00 | 0.02 | 0.06-0.04 | 2.71+1.45 | 4.16 | | | | | |
| 2.59 | 0.55-0.05 | 0.50 | 0.00-0.00 | 0.00-0.00 | 0.02 | 0.06-0.04 | 2.71+1.45 | 4.16 | 66.3 | 68.0 | 162.6 | | |
| 3.02 | 0.55-0.05 | 0.50 | 0.00-0.00 | 0.00-0.00 | 0.02 | 0.06-0.04 | 2.71+1.45 | 4.16 | — | — | — | Barometer | 30.169 |
| 3.05 | 0.55-0.05 | 0.50 | 0.00-0.00 | 0.00-0.00 | 0.02 | 0.06-0.04 | 2.71+1.45 | 4.16 | | | | | |
| 3.08 | 0.55-0.05 | 0.50 | 0.00-0.00 | 0.00-0.00 | 0.02 | 0.06-0.04 | 2.71+1.45 | 4.16 | 66.1 | 68.0 | 162.5 | | |
| 3.11 | 0.55-0.05 | 0.50 | 0.00-0.00 | 0.00-0.00 | 0.02 | 0.06-0.04 | 2.71+1.45 | 4.16 | | | | | |
| 3.14 | 0.55-0.05 | 0.50 | 0.00-0.00 | 0.00-0.00 | 0.02 | 0.06-0.04 | 2.71+1.45 | 4.16 | | | | | |
| 3.17 | 0.55-0.05 | 0.50 | 0.00-0.00 | 0.00-0.00 | 0.02 | 0.06-0.04 | 2.70+1.44 | 4.14 | 65.9 | 68.0 | 161.7 | Barometer | 30.167 |
| 3.20 | 0.55-0.05 | 0.50 | 0.00-0.00 | 0.00-0.00 | 0.02 | 0.06-0.04 | 2.69+1.43 | 4.12 | — | — | — | Barometer | 30.167 |
| 3.23 | 0.55-0.05 | 0.50 | 0.00-0.00 | 0.00-0.00 | 0.02 | 0.06-0.04 | 2.70+1.44 | 4.14 | | | | | |
| 3.26 | 0.55-0.05 | 0.50 | 0.00-0.00 | 0.00-0.00 | 0.02 | 0.06-0.04 | 2.69+1.43 | 4.12 | 66.3 | 68.0 | 162.3 | | |
| 3.29 | 0.55-0.05 | 0.50 | 0.00-0.00 | 0.00-0.00 | 0.02 | 0.06-0.04 | 2.69+1.44 | 4.13 | | | | | |
| 3.32 | 0.55-0.05 | 0.50 | 0.00-0.00 | 0.00-0.00 | 0.02 | 0.06-0.04 | 2.69+1.44 | 4.13 | 67.2 | 68.0 | 162.5 | | |
| 3.35 | 0.55-0.05 | 0.50 | 0.00-0.00 | 0.00-0.00 | 0.02 | 0.06-0.04 | 2.69+1.44 | 4.13 | | | | | |
| 3.38 | 0.55-0.05 | 0.50 | 0.00-0.00 | 0.00-0.00 | 0.02 | 0.06-0.04 | 2.69+1.44 | 4.13 | | | | | |
| 3.41 | 0.55-0.05 | 0.50 | 0.00-0.00 | 0.00-0.00 | 0.02 | 0.06-0.04 | 2.69+1.44 | 4.13 | | | | | |
| 3.44 | 0.55-0.05 | 0.50 | 0.00-0.00 | 0.00-0.00 | 0.02 | 0.06-0.04 | 2.70+1.44 | 4.14 | 66.7 | 68.0 | 162.2 | $\begin{cases} 1.732 \\ 1.735 \\ 1.738 \end{cases}$ | $\begin{cases} 1.984 \\ 1.980 \\ 1.976 \end{cases}$ |
| Totals | — | — | — | — | — | — | — | — | — | — | — | 0.3217 | |
| Means | — | 0.50 | — | — | 0.02 | — | — | 4.143 | 66.4 | 68.0 | 162.4 | 0.3217/54 | |
| Corrected for scale errors | 0.50 | — | — | — | 0.02 | — | — | — | 66.6 | 68.8 | 161.2 | | |
| Corrected for temperatures and absolute pressures | 30.58 | — | 30.10 | — | 30.12 | — | — | — | — | — | — | Barometer | 30.100 |

$$p_0 - p_1 = 4.143 \times 0.869 = 0.2654 \text{ ins. Hg.}$$
$$p_0 - p_1 = 13.596 \times 1.0018 = 0.2654 \text{ ins. Hg.}$$
$$\therefore \mu = 0.00000495 \text{ foot-pound-weight-second unit.}$$

$$p_0 + \frac{p_1}{2} = 30.26 \text{ ins. Hg.}$$
$$w = 0.3217 \times 30.58 \times 0.922$$
$$= 54 \times 60 \times 30.26 \times 0.928$$
$$= 0.0001170 \text{ cubic foot second.}$$

of 30 seconds. The length of time occupied in each experiment varied with the velocity of flow, from 30 minutes to two hours, the average time being about one hour.

A few experiments carried out above the critical velocity in the second tube indicated the similarity of the law governing unsteady flow in the two tubes, while the results of these being plotted with those of a second series of experiments carried out with low-pressure differences (see fig. 3) indicated that a pressure difference of about 0.4 inch of mercury (5.4 inches of water), was necessary to produce unsteady motion. After this, all the experiments were carried out with pressure differences of about 4 inches of water. In the latter series of experiments the volume of air passing per second was measured from the high-pressure reservoir alone, this being found to give perfectly satisfactory results.

A typical experiment is here given. From the experimental figures, the mean values of $p_0 - p_1$; p_0 ; p_1 ; and $\frac{1}{2}(p_0 + p_1)$ or p_m were obtained and corrected for scale errors, temperature, and the barometric height.

The mean volume passing through the tube at the mean pressure p_m and coil temperature was calculated from the mean of the volumes obtained from Reservoirs I and II at their respective mean pressures and temperatures, and in the latter series of experiments, from the readings from No. I reservoir alone. The flow per second is w , = $V/(\text{duration of experiment})$ in cubic feet.

6. *Results of the Experiments.*

The primary results required from each experiment are values of the pressures p_0 and p_1 at the ends of the experimental tube, w the quantity flowing through the tube at the mean pressure $\frac{1}{2}(p_0 + p_1)$ or p_m , and the temperature of the air in the tube. In the following Tables I to VI are placed values of $p_0 - p_1$ and p_m , from which p_0 and p_1 can be calculated for each experiment, together with the flux w , the temperature and the calculated value of μ obtained from equation (1). Values of μ so obtained have been given from experiments when the velocity of flow is above or near the critical velocity; such values, however, have only been used to assist in determining the critical velocity, and they have been placed in italics.

Table I.—Results of Dr. Grindley's Experiments, made for the most part at Velocities of Flow above the Critical Velocity.

| No. of experiment. | Temperature. | $\rho_0 - \rho_1$ (ins. Hg). | $\frac{1}{2}(p_0 + p_1)$. | w (cub.ft.persec.). | μ (foot-pound-weight-second units). |
|--------------------|--------------|---------------------------------|----------------------------|--------------------------|--|
| 6 | 63.5 | 0.556 | 29.92 | 0.000277 | 0.000000409 |
| 5 | 63.5 | 0.557 | 36.05 | 282 | 403 |
| 8 | 61.5 | 0.710 | 30.04 | 347 | 418 |
| 9 | 61.5 | 0.747 | 37.55 | 362 | 422 |
| 4 | 63.5 | 0.804 | 29.98 | 377 | 435 |
| 12 | 66.2 | 1.208 | 30.58 | 541 | 456 |
| 10 | 60.2 | 1.488 | 31.04 | 649 | |
| 13 | 66.2 | 1.824 | 31.08 | 749 | |
| 11 | 60.2 | 2.324 | 31.50 | 924 | |
| 2 | 66.5 | 2.616 | 35.43 | 970 | |
| 14 | 69.2 | 2.910 | 31.96 | 0.001073 | |
| 3 | 66.5 | 3.411 | 33.36 | 1200 | |
| 15 | 69.2 | 4.185 | 32.92 | 1422 | |
| 16 | 74.0 | 4.892 | 33.06 | 1584 | 0.000000630 |
| 7 | 63.5 | 5.421 | 32.61 | 1725 | 642 |
| 1 | 66.5 | 5.474 | 31.08 | 1767 | 633 |
| | | | | | |
| 26 | 73.7 | 0.367 | 30.52 | 0.000208 | 0.000000359 |
| 23 | 73.5 | 0.464 | 30.58 | 244 | 387 |
| 25 | 73.5 | 0.785 | 30.89 | 385 | 415 |
| 18 | 73.5 | 0.936 | 30.84 | 443 | 430 |
| 24 | 73.5 | 1.140 | 31.28 | 519 | |
| 27 | 75.6 | 1.149 | 31.36 | 512 | |
| 17 | 73.3 | 1.304 | 31.23 | 584 | |
| 20 | 74.1 | 1.807 | 31.87 | 744 | |
| 29 | 75.7 | 1.812 | 32.15 | 730 | |
| 31 | 76.5 | 1.964 | 32.52 | 798 | |
| 28 | 75.5 | 2.143 | 32.71 | 845 | |
| 21 | 74.5 | 2.584 | 32.98 | 986 | |
| 33 | 77.0 | 2.685 | 33.70 | 0.001012 | |
| 30 | 75.9 | 2.820 | 33.71 | 1051 | 0.000000547 |
| 32 | 76.8 | 3.051 | 34.20 | 1117 | 557 |
| 34 | 77.0 | 3.217 | 34.57 | 1171 | 560 |
| | | | | | |
| 51 | 32.0 | 0.444 | 30.58 | 0.000237 | 0.000000360 |
| 52 | 32.0 | 0.586 | 30.63 | 302 | 395 |
| 46 | 32.0 | 0.734 | 30.82 | 364 | 410 |
| 43 | 32.0 | 0.774 | 30.70 | 373 | 422 |
| 35 | 32.0 | 0.800 | 30.64 | 405 | |
| 47 | 32.0 | 0.887 | 30.86 | 427 | |
| 38 | 33.0 | 1.059 | 30.79 | 489 | |
| 44 | 32.0 | 1.173 | 31.08 | 532 | |
| 50 | 32.0 | 1.190 | 31.00 | 541 | |
| 41 | 32.0 | 1.358 | 31.07 | 592 | |
| 54 | 32.0 | 1.418 | 31.08 | 627 | |
| 45 | 32.0 | 1.637 | 31.31 | 699 | |
| 36 | 32.0 | 1.653 | 31.13 | 703 | |
| 40 | 32.0 | 2.036 | 31.47 | 829 | |
| 48 | 32.0 | 2.070 | 31.57 | 839 | |
| 49 | 32.0 | 2.218 | 31.64 | 890 | |
| 53 | 32.0 | 2.262 | 31.57 | 895 | 0.000000514 |
| 37 | 32.0 | 2.498 | 31.64 | 974 | 522 |
| 42 | 32.0 | 2.733 | 31.87 | 0.001030 | 540 |

Table I—*continued.*

| No. of experiment. | Temperature. | $p_0 - p_1$ (ins. Hg.). | $\frac{1}{2}(p_0 + p_1)$. | w (cub. ft. per sec.). | μ (foot-pound-weight-second units). |
|--------------------|--------------|----------------------------|----------------------------|-----------------------------|--|
| 68 | 212° 0 | 0·3672 | 29·69 | 0·000161 | 0·000000468 |
| 64 | 212° 0 | 0·4083 | 30·65 | 176 | 476 |
| 67 | 212° 0 | 0·478 | 29·83 | 208 | 472 |
| 62 | 212° 0 | 0·538 | 31·10 | 232 | 475 |
| 58 | 212° 0 | 0·709 | 30·94 | 304 | 479 |
| 55 | 212° 0 | 0·708 | 30·99 | 306 | |
| 65 | 212° 0 | 1·135 | 30·18 | 473 | |
| 56 | 212° 0 | 1·217 | 31·25 | 489 | |
| 61 | 212° 0 | 1·215 | 31·14 | 494 | |
| 57 | 212° 0 | 1·652 | 31·43 | 641 | |
| 59 | 212° 0 | 1·672 | 31·88 | 647 | 0·000000530 |
| 63 | 212° 0 | 1·998 | 31·57 | 749 | 546 |
| 60 | 212° 0 | 2·484 | 31·71 | 898 | 567 |

Table II.—Results of Mr. Gibson's Experiments above the Critical Velocity.

| No. of experiment. | Temperature. | $p_0 - p_1$ (ins. Hg.). | $\frac{1}{2}(p_0 + p_1)$. | w . |
|--------------------|--------------|-------------------------|----------------------------|----------|
| 118 | 32° 2° F. | 0·518 | 30·00 | 0·000255 |
| 119 | 32° 2 | 0·553 | 29·69 | 270 |
| 120 | 32° 2 | 0·5585 | 35·77 | 263 |
| 121 | 32° 0 | 0·9105 | 30·91 | 398 |
| 122 | 32° 0 | 0·603 | 30·78 | 274 |
| 71 | 60° 0 | 0·454 | 29·99 | 0·000193 |
| 72 | 60° 0 | 0·4815 | 30·34 | 243 |
| 73 | 60° 0 | 0·528 | 29·51 | 303 |
| 74 | 60° 0 | 0·538 | 30·03 | 260 |
| 75 | 60° 0 | 0·6415 | 29·08 | 298 |
| 76 | 60° 0 | 0·724 | 30·55 | 354 |
| 77 | 60° 0 | 0·892 | 30·37 | 405 |
| 78 | 60° 0 | 1·104 | 30·06 | 489 |
| 79 | 60° 0 | 1·544 | 31·06 | 630 |
| 104 | 212° 0 | 0·455 | 26·54 | 0·000188 |
| 105 | 212° 0 | 0·455 | 29·99 | 191 |
| 106 | 212° 0 | 0·419 | 30·48 | 212 |
| 107 | 212° 0 | 0·588 | 40·01 | 242 |
| 108 | 212° 0 | 0·741 | 27·15 | 308 |

Table III.—Results of Mr. Gibson's Experiments below the Critical Velocity.

| No. of experiment. | Temperature. | $p_0 - p_1$ (ins. Hg). | $\frac{1}{2} (p_0 + p_1)$. | w (cubic feet per second). | μ (in foot-pound-weight-second units). |
|--------------------|--------------|---------------------------|-----------------------------|------------------------------|--|
| 123 | 32·2° F. | 0·1740 | 30·00 | 0·0000907 | 0·000000357 |
| 124 | 32·1 | 0·2400 | 30·05 | 1253 | 356 |
| 125 | 32·1 | 0·1883 | 30·02 | 0962 | 357 |
| 126 | 32·1 | 0·2984 | 30·08 | 1582 | 351 |
| 127 | 32·1 | 0·2997 | 30·09 | 1550 | 360 |
| 128 | 32·0 | 0·2240 | 29·90 | 1280 | 352 |
| 129 | 32·0 | 0·1879 | 29·90 | 1017 | 357 |
| 130 | 32·0 | 0·1282 | 29·84 | 0710 | 351 |
| 131 | 32·0 | 0·4378 | 29·69 | 2290 | 356 |
| 132 | 32·0 | 0·2413 | 29·83 | 1266 | 355 |
| 133 | 32·0 | 0·0904 | 29·66 | 0470 | 358 |
| 134 | 32·0 | 0·1994 | 30·09 | 1047 | 355 |
| 135 | 32·0 | 0·1399 | 30·30 | 0756 | 356 |
| 136 | 32·0 | 0·2041 | 26·80 | 1100 | 358 |
| 137 | 32·0 | 0·1956 | 26·12 | 1067 | 354 |
| 138 | 32·0 | 0·2025 | 30·18 | 1118 | 351 |

Mean value of $\mu = 0·0000003553$.

Greatest positive variation from mean 1·35 per cent.
 „ negative „ „ 1·15 „

Table IV.

| No. of experiment. | Temperature. | $p_0 - p_1$ (ins. Hg). | $\frac{1}{2} (p_0 + p_1)$. | w (cubic feet per second). | μ (foot-pound-weight-second units). |
|--------------------|--------------|---------------------------|-----------------------------|------------------------------|---|
| 80 | 60·3° F. | 0·2707 | 29·90 | 0·0001346 | 0·000000375 |
| 81 | 60·0 | 0·3147 | 29·83 | 1591 | 369 |
| 82 | 60·0 | 0·3069 | 29·84 | 1535 | 373 |
| 83 | 60·2 | 0·3273 | 29·75 | 1638 | 374 |
| 84 | 60·0 | 0·3377 | 29·85 | 1685 | 374 |
| 85 | 59·0 | 0·2414 | 28·49 | 1263 | 369 |
| 86 | 58·8 | 0·2786 | 34·83 | 1465 | 369 |
| 87 | 58·0 | 0·2140 | 34·61 | 1102 | 371 |
| 88 | 60·0 | 0·0606 | 29·66 | 0301 | 375 |
| 89 | 60·0 | 0·1149 | 29·85 | 0600 | 370 |
| 90 | 60·0 | 0·1586 | 30·04 | 0815 | 374 |
| 91 | 60·0 | 0·2357 | 29·16 | 1225 | 372 |
| 92 | 60·0 | 0·2418 | 30·06 | 1260 | 371 |

Mean value of $\mu = 0·0000003720$.

Greatest positive variation from mean 0·91 per cent.
 „ negative „ „ 0·81 „

Table V.

| No. of experiment. | Temperature. | $p_0 - p_1$ (ins. Hg.). | $\frac{1}{2} (p_0 + p_1)$. | w (cubic feet per second). | μ (foot-pound-weight-second units). |
|--------------------|--------------|----------------------------|-----------------------------|------------------------------|---|
| 93 | 212° F. | 0.2153 | 30.04 | 0.0000807 | 0.000000446 |
| 94 | 212 | 0.2301 | 40.35 | 0966 | 447 |
| 95 | 212 | 0.2512 | 29.12 | 1049 | 450 |
| 96 | 212 | 0.2578 | 39.82 | 1082 | 447 |
| 97 | 212 | 0.2597 | 30.81 | 1082 | 451 |
| 98 | 212 | 0.2945 | 30.48 | 1237 | 447 |
| 99 | 212 | 0.2978 | 29.96 | 1115 | 447 |
| 100 | 212 | 0.3118 | 42.37 | 1320 | 443 |
| 101 | 212 | 0.3387 | 44.26 | 1425 | 446 |
| 102 | 212 | 0.4616 | 40.29 | 1940 | 447 |
| 103 | 212 | 0.4552 | 30.95 | 1908 | 448 |

Mean value of $\mu = 0.0000004473$.

Greatest positive variation from mean 0.79 per cent.

" negative " " 0.85 "

Table VI.

| No. of experiment. | Temperature. | $p_0 - p_1$ (ins. Hg.). | $\frac{1}{2} (p_0 + p_1)$. | w (cubic feet per second). | μ (foot-pound-weight-second units). |
|--------------------|--------------|----------------------------|-----------------------------|------------------------------|---|
| 109 | 35.0° F. | 0.2024 | 30.33 | 0.0001058 | 0.000000356 |
| 110 | 36.5 | 0.2025 | 29.96 | 1080 | 349 |
| 111 | 37.5 | 0.1015 | 30.02 | 0529 | 357 |
| 112 | 38.0 | 0.1705 | 37.77 | 0883 | 360 |
| 113 | 39.4 | 0.3424 | 29.78 | 1770 | 360 |
| 114 | 40.7 | 0.1927 | 29.68 | 0956 | 361 |
| 115 | 41.2 | 0.3072 | 29.92 | 1560 | 367 |
| 116 | 41.4 | 0.3065 | 29.92 | 1573 | 363 |
| 117 | 42.9 | 0.3066 | 29.90 | 1580 | 364 |
| 139 | 48.5 | 0.3005 | 29.88 | 1543 | 363 |
| 140 | 53.8 | 0.3034 | 29.69 | 1530 | 369 |
| 141 | 54.0 | 0.3288 | 29.67 | 1663 | 369 |
| 142 | 54.0 | 0.2942 | 29.73 | 1485 | 369 |
| 144 | 74.1 | 0.3406 | 30.08 | 1670 | 381 |
| 145 | 74.7 | 0.1773 | 29.82 | 0866 | 382 |
| 146 | 77.5 | 0.3068 | 30.03 | 1492 | 384 |
| 147 | 77.5 | 0.3451 | 30.07 | 1686 | 382 |
| 149 | 91.2 | 0.3297 | 30.18 | 1590 | 387 |
| 150 | 91.4 | 0.3023 | 30.01 | 1471 | 384 |
| 151 | 95.6 | 0.3504 | 29.93 | 1656 | 395 |
| 152 | 96.2 | 0.2513 | 29.87 | 1196 | 393 |
| 153 | 95.7 | 0.3425 | 29.84 | 1646 | 389 |
| 154 | 98.7 | 0.3031 | 29.81 | 1446 | 391 |
| 155 | 118.7 | 0.2977 | 29.77 | 1377 | 404 |
| 156 | 120.0 | 0.3057 | 29.74 | 1443 | 395 |
| 157 | 119.8 | 6.2878 | 29.72 | 1337 | 403 |
| 158 | 121.9 | 0.3189 | 29.21 | 1474 | 405 |
| 159 | 120.1 | 0.3334 | 30.33 | 1542 | 404 |
| 160 | 120.0 | 0.2199 | 30.28 | 1002 | 411 |
| 161 | 134.1 | 0.3178 | 30.31 | 1446 | 411 |
| 162 | 134.4 | 0.3160 | 30.14 | 1439 | 411 |
| 163 | 135.2 | 0.3107 | 29.81 | 1407 | 413 |

Table VI—*continued*.

| No. of experiment. | Temperature. | $p_0 - p_1$ (ins. Hg). | $\frac{1}{2}(p_0 + p_1)$. | w (cubic feet per second). | μ (foot-pound-weight-second units). |
|--------------------|--------------|---------------------------|----------------------------|------------------------------|---|
| 164 | 135.9° F. | 0.3241 | 29.82 | 0.0001460 | 0.000000415 |
| 165 | 141.8 | 0.2894 | 30.27 | 1308 | 414 |
| 166 | 142.5 | 0.3197 | 30.19 | 1429 | 419 |
| 167 | 143.9 | 0.3229 | 30.30 | 1454 | 416 |
| 168 | 150.3 | 0.3179 | 29.70 | 1417 | 420 |
| 169 | 151.4 | 0.3390 | 30.31 | 1486 | 423 |
| 170 | 151.7 | 0.3084 | 29.68 | 1383 | 418 |
| 171 | 150.9 | 0.2873 | 30.66 | 1302 | 413 |
| 172 | 161.2 | 0.2655 | 30.26 | 1170 | 425 |
| 173 | 163.0 | 0.3312 | 30.30 | 1457 | 426 |
| 174 | 163.5 | 0.2982 | 30.28 | 1294 | 431 |
| 175 | 167.7 | 0.2965 | 31.53 | 1281 | 433 |
| 176 | 175.0 | 0.2392 | 30.20 | 1244 | 436 |
| 177 | 178.8 | 0.3786 | 29.68 | 1636 | 434 |
| 178 | 179.1 | 0.3070 | 29.64 | 1346 | 428 |
| 179 | 180.0 | 0.3116 | 30.29 | 1336 | 437 |
| 180 | 182.1 | 0.3080 | 30.13 | 1322 | 437 |
| 181 | 185.4 | 0.2849 | 30.04 | 1221 | 438 |
| 182 | 198.6 | 0.2973 | 30.28 | 1258 | 444 |
| 183 | 199.2 | 0.2943 | 30.28 | 1243 | 444 |
| 184 | 204.0 | 0.3290 | 30.19 | 1383 | 447 |
| 185 | 204.7 | 0.2929 | 29.99 | 1234 | 445 |

7. The Determination of the Critical Velocity.

The critical velocity of flow through the pipe at any particular temperature can best be obtained by calculating the value of μ from the figures given in Table I, on the assumption that equation (1) holds for these experiments, and comparing these incorrect values of the coefficient of viscosity with the correct values given by Tables III, IV, and V. If all these values of μ are plotted with the flux w , it should be easy to determine the value of w at which the value of μ begins to increase.

It would appear that the value of w at the critical velocity was between 0.00017 and 0.00018 cubic feet per second, which gives for the critical velocity a mean value of approximately 1.95 feet per second. Its accurate determination was difficult, but the results indicate that for this pipe the critical velocity lies between 1.9 and 2.0 feet per second.

The results also show that if there is any variation in the value of this critical velocity with temperature it cannot be very great.

8. The Coefficient of Viscosity and its Variation with Temperature and Pressure.

A consideration of the kinetic theory of gases led Maxwell* to the conclusion that the coefficient of viscosity of a gas would be independent of

* 'Phil. Mag.,' 1860, vol. 19, p. 20.

the pressure. This deduction, verified by many observers,* receives additional confirmation from the results of Experiments 94, 96, 100, 101, 102, and of Experiments 93, 95, 98, 99.

These are as follows:—

| No. of experiment. | Temperature. | $\frac{1}{2}(p_0 + p_1)$ inches of mercury. | μ (foot-pound-weight-second units). |
|------------------------------------|--------------|---|---|
| | ° F. | | |
| 94 | 212 | 40·3 | 0·000000447 |
| 96 | 212 | 39·8 | 447 |
| 100 | 212 | 42·4 | 444 |
| 101 | 212 | 44·2 | 446 |
| 102 | 212 | 40·3 | 447 |
| Mean value of $\mu = 0·0000004462$ | | | |
| 93 | 212 | 30·0 | 0·000000446 |
| 95 | 212 | 29·1 | 450 |
| 98 | 212 | 30·5 | 447 |
| 99 | 212 | 30·0 | 447 |
| Mean value of $\mu = 0·0000004475$ | | | |

A comparison of these results tends to show that, within the limits of experimental error, the viscosity is independent of the pressure.

To test the variation of μ with temperature in the present experiments, values of $\log \mu$ and of $\log \tau$ have been plotted (fig. 4). From the fact that the plotted points lie on a regular curve and not on a straight line, it is evident that no such law as μ and τ^n , where n is a constant, holds for the range of temperature from $\tau = 493^\circ$ abs. to $\tau = 673^\circ$ abs.

The variation of n in this formula, with temperature, is shown in the following table:—

| Temperature range. | | n . |
|--------------------|---------|-------|
| Absolute. | F. | |
| 493°—521° | 32°—60° | 0·830 |
| 521—551 | 60—90 | 0·811 |
| 551—581 | 90—120 | 0·788 |
| 581—611 | 120—150 | 0·759 |
| 611—641 | 150—180 | 0·666 |
| 641—673 | 180—212 | 0·561 |

* See the 'Physical Review,' vol. 24, p. 335, for a *résumé* of much of the work done in this connection.

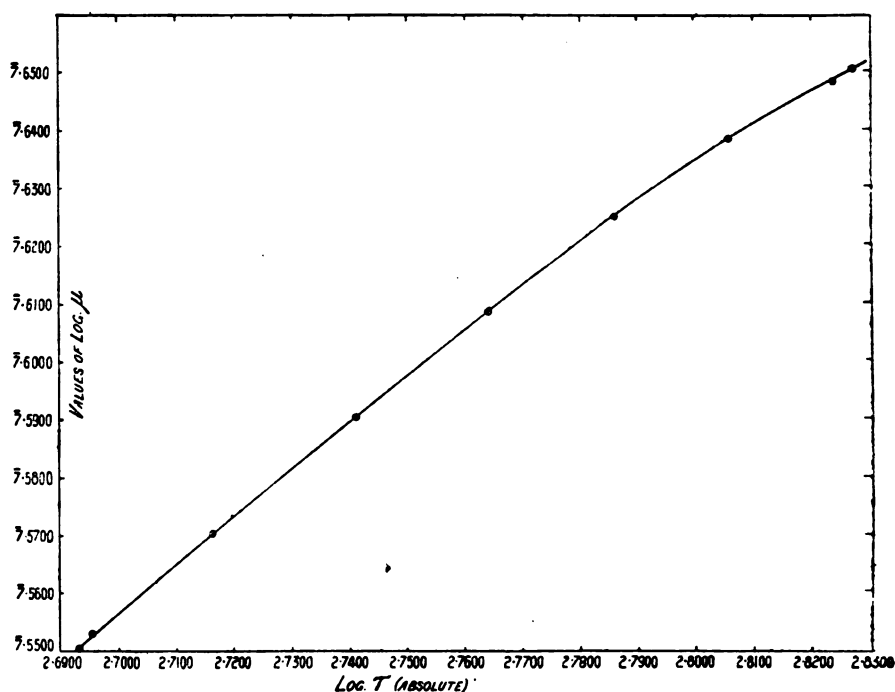


FIG. 4.

Rayleigh,* using the transpiration method, found n to have a mean value of 0.754 between the temperature limits 15° and 100° C. Between the same limits the present experiments show a mean value for $n = 0.727$.

Sutherland† has proposed, and has justified on theoretical grounds, the formula

$$\mu = \frac{K\tau^{\frac{1}{2}}}{1 + C\tau^{-1}},$$

where C and K are constants, and where τ is the absolute temperature, this relation holding for temperatures above the critical within the range of pressures over which Boyle's law is approximately true.

Writing this in the form $\tau = K\tau^{\frac{1}{2}}/\mu - C$, we have a linear equation in τ and $\tau^{\frac{1}{2}}/\mu$. Values of τ and of $\tau^{\frac{1}{2}}/\mu$, as calculated from the present series of experiments, have been plotted in fig. 5, and, by their close coincidence with a straight line, confirm this formula.

The values of K and C most nearly fitting the above equation have been deduced from the results of the whole of the present series of experiments by the method of least squares, the straight line shown in fig. 5 involving these values.

* 'Roy. Soc. Proc.,' 1900, vol. 66, p. 68.

† 'Phil. Mag.,' 1893, vol. 36, p. 507.

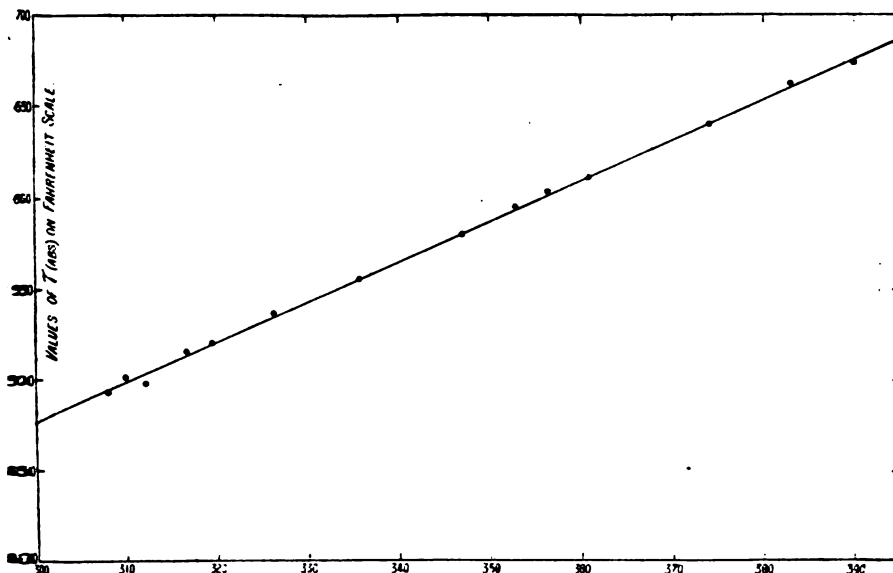


FIG. 5.

These are as follows, the abscissa representing $\tau^{\frac{1}{2}}/10^7\mu$.

| | K. | C. |
|---|-------------------------|-------|
| τ measured on F. scale ($0^\circ \text{ F.} = 461 \text{ abs.}$); μ in foot-pound-weight-second units | 220.7×10^{-10} | 184.5 |
| τ measured on C. scale ($0^\circ \text{ C.} = 274 \text{ abs.}$); μ in foot-pound-weight-second units | 296.0×10^{-10} | 102.5 |
| τ measured on C. scale ($0^\circ \text{ C.} = 274 \text{ abs.}$); μ in absolute foot-pound-weight-second units | 952.0×10^{-9} | 102.5 |
| τ measured on C. scale ($0^\circ \text{ C.} = 274 \text{ abs.}$); μ in absolute C.G.S. units | 141.8×10^{-7} | 102.5 |

the plotted points in fig. 6 show the experimental variation of viscosity temperature, while the full line curve shows the graph of

$$\mu = \frac{220.7 \times 10^{-10} \tau^{\frac{1}{2}}}{1 + 184.5 \tau^{-1}}.$$

maximum experimental deviation from this law is 1.3 per cent.

only other experiments known to the authors, from which the value as been determined, are those of Holman* and of Barus.† In those man, over a temperature range of 14° to $124^\circ.4 \text{ C.}$, C was found to be value 113, the units being on the absolute C.G.S. scale, while in

* 'Phil. Mag.,' 5th series, 1886, vol. 21, p. 199.

† 'Am. Journ. Sci.,' 3rd series, vol. 135.

the experiments of Barus the value of C , with the same units, and between the temperature limits 442° and 1216° C., was found to be 102, as compared with 102.5 in the present experiments.

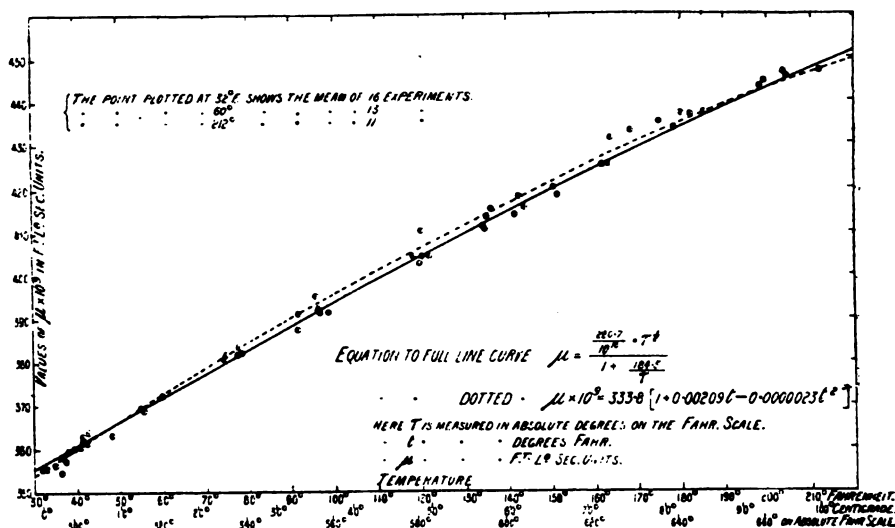


FIG. 6.

For comparison with the published results of other experimenters, the results of the present experiments have been expressed in the form

$$\mu = a \{1 + bt + ct^2\}.$$

The constants in this equation, the graph of which is shown in dotted lines in fig. 6, are as follows, t being measured in degrees Centigrade:—

| | a . | b . | c . |
|---|------------------------|---------|-----------|
| μ in foot-pound-weight-second units | 333.8×10^{-9} | 0.00209 | 0.0000028 |
| μ in "absolute" foot-pound-second " | 355.8×10^{-9} | 0.00329 | 0.0000070 |
| μ in absolute " C.G.S. units | 114.2×10^{-7} | 0.00329 | 0.0000070 |
| " C.G.S. units | 170.2×10^{-6} | 0.00329 | 0.0000070 |

as compared with Holman's,

$$\mu = 171.55 \{1 + 0.002751t - 0.00000034t^2\} 10^{-6} \text{ abs. C.G.S. units.}$$

Tomlinson,* with a temperature range of from $9^{\circ}97$ C. to $14^{\circ}63$ C., adopted this same law of temperature variation. The value of μ at Tomlinson's mean temperature, $11^{\circ}8$ C., as calculated by the author's formula, agrees within one-tenth of 1 per cent. with the value as experimentally determined by Tomlinson.

* 'Phil. Trans.,' 1886, part 2, p. 767.

The following table, showing values of μ at 0° C., as obtained by various observers, may be of interest :—

| Observer | Meyer.* | Puluj.* | Schneebeli.† | Obermayer.† | Holman. | Tomlinson. | The authors. |
|-------------------------|-----------|-----------|--------------|-------------|-----------|------------|--------------|
| Value of μ at 0° C. | 0·0001727 | 0·0001798 | 0·0001707 | 0·0001705 | 0·0001715 | 0·0001715 | 0·0001702 |

9. *The Determination of the Frictional Resistances at Velocities of Flow greater than the Critical.*

As the experiments proceeded it was observed that the quantity of air through the tube in any experiment could not be estimated previously by calculation from known formulæ containing empirical constants; and hence the experimental figures were used to obtain, by using the usual equation (4), p. 119, values of the coefficient ζ . Now, if the laws of resistance are in reality those used in demonstrating equation (4), it follows that ζ should be practically a constant for experiments with air in the same tube and at the same constant temperature, unless the influence of tube diameter is far greater than at present suspected.

A few values of ζ , calculated by using equation (4), are here given :—

| No. of experiment. | ζ . | u_m —the mean velocity of air in the tube in feet per second. | p_m —the mean pressure in the tube in inches Hg. |
|--------------------|-----------|---|--|
| 6 | 0·0837 | 3·12 | 29·92 |
| 5 | 0·0675 | 3·18 | 36·05 |
| 9 | 0·0529 | 4·07 | 37·55 |
| 4 | 0·0654 | 4·25 | 29·98 |
| 12 | 0·0467 | 6·09 | 30·58 |
| 13 | 0·0365 | 8·43 | 31·03 |
| 2 | 0·0272 | 10·9 | 35·43 |
| 3 | 0·0246 | 13·5 | 33·87 |
| 7 | 0·0194 | 19·4 | 32·61 |
| 1 | 0·0196 | 19·9 | 31·08 |

These values of ζ are considerably higher than those given by previous authors, which is possibly accounted for by the small diameter of the pipe, and a very large variation in its value with the mean velocity u_m is shown, the connection between ζ and u_m being shown by the curve in fig. 7.

* 'Phil. Mag.,' 1886, vol. 21, p. 220.

† 'Archives Sci. Phys. Nat.,' 1885, vol. 14.

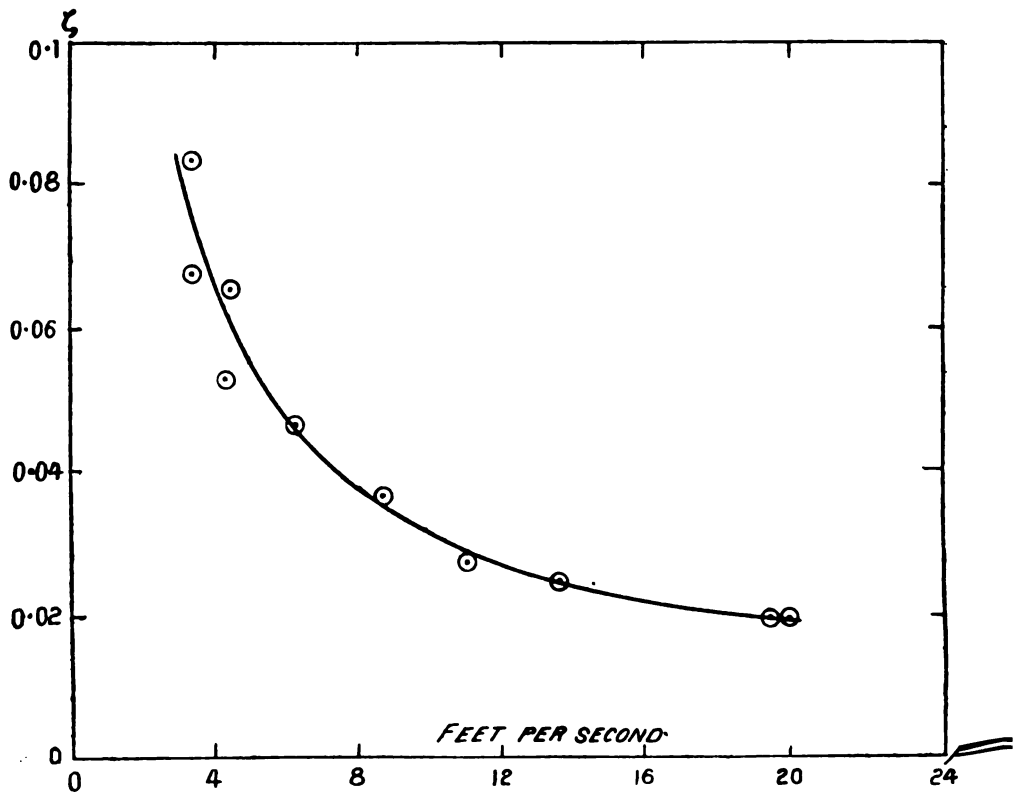


FIG. 7.

Unwin* deduces values of ζ from Riedler's experiments on a pipe 11½ inches diameter, and gives varying values of ζ from 0.00184 to 0.00449. From Stockalper's experiments Unwin deduces the values $\zeta = 0.00449$ from a pipe 0.492 foot diameter, and $\zeta = 0.00377$ from a pipe 0.656 foot diameter, and he gives from these results a formula for calculating ζ for pipes of different diameters in form—

$$\zeta = 0.0027 \left(1 + \frac{3}{10d} \right).$$

For a pipe 1/8 of an inch diameter this formula would give $\zeta = 0.0805$, a value which would be obtained from the present experiments if the mean velocity u_m was a little over 3 feet per second. The variation in the value of ζ with u_m is, however, too great to permit of Unwin's formula being used for so small a pipe.

* 'Min. Proc. I.C.E.,' vol. 106, p. 190.

It would be interesting to use the experimental figures to find whether the variation in the frictional resistances is best represented by u^2 or by some other power of u . An examination of the curve in fig. 7 will show that the points lying above or below the mean curve correspond to the value of p_m in the experiments they represent, being below or above an average value of p_m , and it apparently indicates that the frictional resistances may bear some unexpressed relation to the pressure in the gas.

Whether a pressure variation is real or not, it appears reasonable to assume that ζ should have a more constant value for the particular pipe used than that shown in the last table if the resistances do vary as the assumed square of the velocity. While the whole question can only be definitely settled by making experiments similar to the present ones on pipes of different diameters, still it is interesting and useful to observe what power of the mean velocity in the formula for the frictional resistances would give a constant value of a coefficient of friction for this pipe.

It was found impossible to obtain this constant value without reconstructing the primary formula as shown on pp. 120 and 121, and use was, therefore, made of the general equation (12), p. 121, which can be put in the form

$$f = C \cdot \frac{p_0^{n-r+1} - p_1^{n-r+1}}{p_m^n w^n}, \quad (13)$$

where C is a constant in any series of experiments on the same tube with air at the same constant temperature. Values of n and r were sought which would make the factor $(p_0^{n-r+1} - p_1^{n-r+1})/p_m^n w^n$ a constant during any such series of experiments, in which case f would also be constant.

The determination of these exponents involved much time and labour, but their values appear to be

$$n = 1.25 \quad \text{and} \quad r = 0. \quad (14)$$

This value of n is not likely to be in error by as much as 1 per cent., and $r = 0$ is the most probable value of r , though any very small value of r would serve. This value of r is very peculiar, since it leads to the result that the frictional resistances are independent of the pressure in the gas; this point will be referred to later.

With these values of n and r , the values of $(p_0^{n-r+1} - p_1^{n-r+1})/p_m w$, as calculated from the results of the experiments above the critical velocity at any particular temperature, are practically constant; thus at a mean temperature of 75°·2 F. the greatest variation of the value of this factor from the mean is less than 2·9 per cent.

Using formula (13) to determine values of f , using $n = 1.25$ and $r = 0$, we obtain the following mean results:—

$$\begin{aligned} f &= 0.000215 \text{ at temperature } 32^\circ \text{ F.} \\ f &= 0.000219 \quad \quad \quad \text{,,} \quad \quad \quad 75^\circ.2 \text{ F.} \\ f &= 0.000242 \quad \quad \quad \text{,,} \quad \quad \quad 212^\circ \text{ F.} \end{aligned}$$

the units being the foot-pound weight and second.

These values are plotted in fig. 8, showing that the variation in the value of f with temperature Fahr. t can be represented by

$$f = f_0(1 + \alpha t + \beta t^2), \quad (15)$$

where $f_0 = 0.000213$, $\alpha = 0.000295$, and $\beta = 0.0000017$.

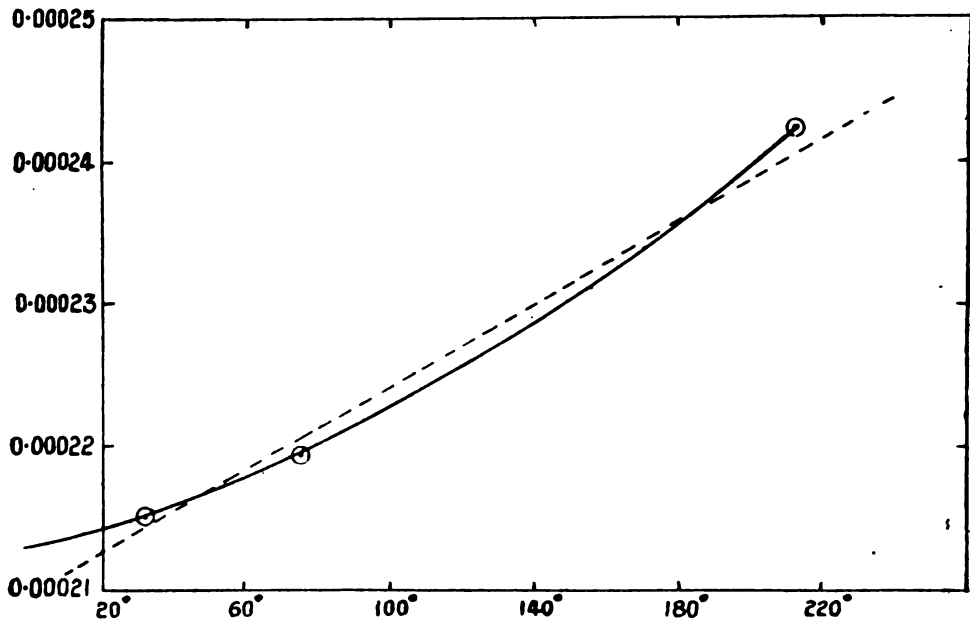


FIG. 8.

The chief conclusions, therefore, to be drawn from these numbers are that for this particular size of tube the frictional resistances are better represented by a velocity variation represented by $w^{1.25}$ than by the usually accepted w^2 , and, further, that the frictional resistances do not vary with the pressure of the air in the tube.

Though this variation of the frictional resistances with the velocity is unusual, and requires further evidence on pipes of other diameters before it could be accepted, it is worthy of note that if the formula (12), which can be put in the form

$$f = \frac{0.0824}{l} \cdot \frac{d^{3.5}}{w^{1.25}} \cdot \frac{p_0^{2.25} - p_1^{2.25}}{p_m^{1.25}}, \quad (16)$$

is applied to determine f , using the results of Riedler's experiments previously mentioned,* a mean value of f calculated from all the experiments there quoted is 0.000217, while the value of f calculated from (15) with $t = 50^\circ$ would also be 0.000217.

From Stockalper's experiments, using the only figures given in the above paper, f would have a mean value 0.000182, but omitting one quite irregular experimental result we should get a mean value 0.000201.

These values are remarkably near those given from the present experiments, considering that the mean pressures in Riedler's experiments were about 100 lbs. per square inch, with velocities ranging from 10 to 24 feet per second (similar to those in the present experiments), and on a pipe $11\frac{3}{4}$ inches diameter.

* 'Min. Proc. I.C.E.,' vol. 105.

Exterior Ballistics. (No. 2.)

By GEORGE FORBES, F.R.S.

(Received November 6,—Read December 12, 1907.)

In a previous communication to the Royal Society,* the author exhibited a curve which may be described as the characteristic curve of any gun, charge and projectile, in which the abscissæ are ranges, and ordinates are tangents of the angles of elevation, or simply these angles when they are small.

That communication contained (1) a geometrical construction for deducing a new characteristic curve when the air density or the gun's calibre is changed; (2) the analytical proof of that law; (3) the law for deducing a new characteristic curve when the muzzle velocity is changed; (4) a comparison of range-tables showing how, by help of these laws, from the characteristic curve for a gun of any calibre and muzzle velocity, to deduce the curve for a gun of any other calibre and muzzle velocity; and (5) empirical formulæ enabling a practical gunsight to be so constructed that when set for true range, it is also set for the true elevation, whatever the calibre of the gun, the muzzle velocity, the air density, and the rate of change of range may be.

6. At a conversazione of the Royal Society last year, a model of this gunsight, made by Sir W. G. Armstrong, Whitworth, and Co., was shown, and later a complete sight for a 6-inch gun was made by the same firm, and was tested and approved of by the Naval experts at Portsmouth, but it has not been adopted for the British Navy. The author had designed this sight for use in connection with a range-finder, and also with a new range-keeping instrument, and a mechanical transmission of ranges to the gunsights, so designed that the guns of all calibres are kept by a motor continuously set for the varying range, while the speed of the motor is checked by occasional observations of the range. The advantages claimed for this system of gun-sighting are: (1) All guns being set to the true range, a ship may carry guns of various calibres, and the abolition of the secondary armament in our battleships is unnecessary, in so far as fire-control is a consideration. (2) The officers, during an action, are relieved from much brain-work. (3) The best brains of the ship do not need to be concentrated on a platform at the mast-head. (4) Surrender of a ship when that mast is shot away becomes unnecessary, because control of all of the ship's guns can be

* 'Roy. Soc. Proc.,' January, 1905.

carried on from any turret. These advantages can be secured only by using a sight like the one first exhibited by the author to the Royal Society, which is always set to the true range, whatever may be the muzzle velocity, air-density, and rate of change of range.

As the author referred to this gunsight in his previous paper on "Exterior Ballistics," he desires thus shortly to record the success that attended its construction, before proceeding now to some new ballistic theorems.

7. *The Angle of Descent.*—A knowledge of the inclination of the trajectory of a shot to the horizontal line at the end of its flight is necessary for estimating the extent of the danger zone. According to the principle of the rigidity of the trajectory, proved in artillery text-books, if the axis of the gun has to be inclined at an angle of elevation α to the line of sight to hit a target at the range R on a horizontal plane, the same setting is correct for any target vertically above the former; so that if the vertical angle between the two target positions be not great, the trajectory is simply raised through that angle. Call this angle $\delta\alpha$, and let $R + \delta R$ be the range on the horizontal plane for the elevation $\alpha + \delta\alpha$. From fig. 1 it is clear

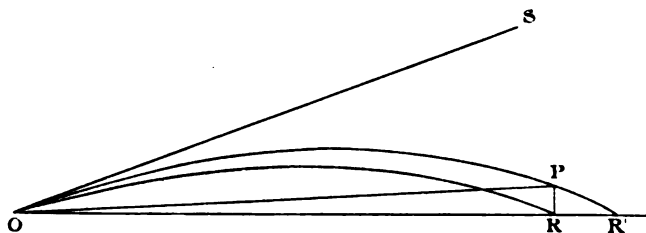


FIG. 1.

that, if $OR = R$ and $OR' = R + \delta R$, and if $SOP = \alpha$ and $POR = \delta\alpha$, and $PR'R = CO$, the angle of descent, when δR and $\delta\alpha$ are reduced indefinitely, then

$$\tan \omega = \frac{PR}{RR'} = R \frac{d\alpha}{dR} \text{ in the limit.}$$

8. The characteristic curve introduced by the author gives the geometrical expression of this law very neatly. In fig. 2, OR is a range and $\tan \alpha = PR$.

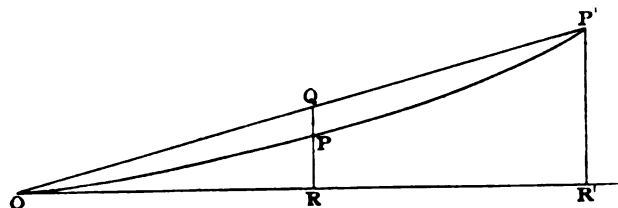


FIG. 2.

Through O draw OQ parallel to the tangent at P, and cutting RP produced in Q. Then

$$\frac{QR}{OR} = \frac{d \cdot PR}{d \cdot OR} = \frac{d \cdot \tan \alpha}{dR} = \frac{1}{\cos^2 \alpha} \cdot \frac{d\alpha}{dR} = \frac{d\alpha}{dR}$$

for moderate elevations; therefore

$$QR = OR \cdot \frac{d\alpha}{dR} = \tan \omega.$$

Thus PR is the angle of elevation and QR the angle of descent, or their tangents.

9. *Corollary*.—If in fig. 2 the line OQ produced cuts the characteristic curve at P', draw P'R' perpendicular to OR produced. If, as a first approximation, the curvature of OPP' be taken as uniform, then OR' = 2OR and P'R' = 2QR. Hence, if the angle of descent be known at any range, twice this angle is approximately the angle of elevation at twice the range. This rule for extending a range-table to longer ranges has long been known as an approximation. The geometrical form of proof shows clearly its limitations.

10. *To trace the trajectory* from the elevations and corresponding ranges given in a range-table:—

Rule: In fig. 3, let OR be the range and SOx the elevation. Take any

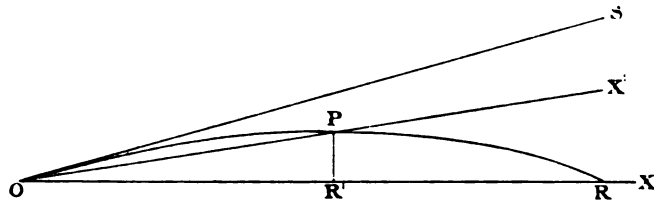


FIG. 3.

other range OR', and draw OX' so that SOX' is the corresponding elevation. Through R' draw R'P vertically, meeting OX' in point P. Then the locus of P is the trajectory.

This follows directly from the principle of rigidity of the trajectory. For if OX' were horizontal, the angle of elevation SOX' would carry the shot to R', and that principle says that when OX' is inclined the shot is carried to the point P. We must not assume, however, a mathematical accuracy in that principle in cases where SOX' is not a small angle. But even where not mathematically exact this construction is very useful.

The Effects of Temperature and Pressure on the Thermal Conductivities of Solids. Part II.—The Effect of Low Temperatures on the Thermal Conductivities of Pure Metals and Alloys.

By CHARLES H. LEES, D.Sc., F.R.S., Professor of Physics in the East London College, University of London.

(Received November 8,—Read December 12, 1907.)

(Abstract.)

The object of the work described in the present paper was to extend the measurements of Thermal Conductivities of Metals and Alloys made by Lorenz, Jäger and Diesselhorst, and others at temperatures between 0° C. and 100° C. down to the temperature of liquid air, and thus provide a means of comparing the Thermal and Electrical Conductivities of these substances over a much wider range of temperature than has hitherto been possible.

The method adopted was a modification of that used originally by Wiedemann and Franz. A rod of the metal, 7 or 8 cm. long, 0.6 cm. in diameter, was placed in the axis of a vertical copper tube of 2.7 cm. internal 3.3 cm. external diameter, 9.5 cm. long, closed at the top. The lower end of the rod fitted into a copper disc, which in its turn fitted into the lower end of the copper tube. The joints were accurately made and were smeared with olive oil to exclude air and improve the thermal contact. The heat which flowed along the rod was supplied electrically by means of a current through a fine platinoid wire wound on a short thin brass sleeve, which was slipped on to the upper end of the rod. The difference of temperatures at two points of the rod, between the heating coil and the point where the rod entered the disc forming the lower end of the tube, was measured by means of two platinum thermometers, the wires of which were wound on two short thin brass sleeves, capable of sliding along the rod. The three sleeves fitted the rod closely, and thermal contact was improved by smearing rod and sleeves with a little olive oil.

The apparatus was placed in a Dewar vacuum vessel, which could be filled with liquid air. When the apparatus had cooled down to the temperature of the liquid, the excess of liquid was poured off, and observations commenced. Owing to the heat supplied to the rod, and the flow of heat from without, the

temperature of the whole apparatus rises, and it is shown in the complete paper under what conditions observations taken under such circumstances can be used to determine conductivities.

In making a determination, the difference of resistance of the two platinum thermometers was first measured with the heating current round the rod zero, then with the current flowing, then again with it zero. The difference between the second and the mean of the first and last gives the difference of resistance due to the flow of heat down the rod.

The instruments used in measuring the watts spent in the heating coils were standardised, and a correction was made for the heat conducted away from the rod along the wires supplying the current and along the wires to the platinum thermometers. The effect of each sleeve on the flow of heat through the rod in its neighbourhood was calculated and allowed for.

The platinum thermometers were standardised by observations of their resistances in steam at about 100°C ., in ice at 0°C ., and in liquid oxygen boiling under a reduced measured pressure. All temperatures are by these means reduced to the standard constant volume hydrogen thermometer.

Resistance coils were standardised by comparison with standards tested at the National Physical Laboratory or at the Reichsanstalt.

The rods used were turned from materials supplied as pure by firms of repute, and have been tested for density and electrical conductivity.

The following table embodies the results obtained, together with those given for higher temperatures by Jäger and Diesselhorst, and it will be seen that they justify the following statements:—

The thermal conductivities of most pure metals decrease as the temperature rises within the range -160° to 100°C .

The thermal conductivities of all alloys tested increase as the temperature rises within the range -160° to 100°C .

Table of Thermal Conductivities of Pure Metals and Alloys between -160° and 18° C., as deduced from the present Experiments, compared with those at 18° and 100° C. given by Jäger and Diesselhorst as the results of their Experiments.

| Substance. | Chemical and physical state. | From the present experiments. | | | | Jäger and Diesselhorst's results. | | Chemical and physical state. |
|-----------------|------------------------------|-------------------------------|---------------------|-------------------|---------------------|-----------------------------------|---------------------|------------------------------|
| | | At -160° C. | At -80° C. | At 0° C. | At $+18^{\circ}$ C. | At 18° C. | At 100° C. | |
| Copper | Pure soft drawn | 1·075 | 0·960 | 0·924 | 0·916 | 0·918 | 0·908 | Pure |
| Silver | 0·999 Ag | 0·998 | 1·006 | 0·981 | 0·974 | 1·006 | 0·992 | 0·9998 Ag |
| Zinc | Pure redistilled cast | 0·278 | 0·269 | 0·269 | 0·268 | 0·265 | 0·262 | Pure cast |
| Cadmium | Ditto | 0·239 | 0·228 | 0·219 | 0·217 | 0·222 | 0·216 | Ditto |
| Aluminium ... | 0·99 Al | 0·514 | 0·498 | 0·502 | 0·504 | 0·480 | 0·492 | 0·99 Al |
| Tin | Pure cast | 0·192 | 0·173 | 0·160 | 0·157 | 0·155 | 0·145 | Pure wire |
| Lead | Pure | 0·092 | 0·085 | 0·084 | 0·083 | 0·083 | 0·082 | Pure |
| Iron | Wrought | 0·152 | 0·150 | 0·147 | 0·147 | 0·144 | 0·143 | 0·9955 Fe |
| Nickel | 0·99 Ni | 0·129 | 0·136 | 0·140 | 0·140 | 0·142 | 0·138 | 0·97 Ni |
| Steel | ... | 0·113 | 0·115 | 0·116 | 0·115 | 0·108 | 0·107 | 0·01 C |
| Brass | ... | 0·181 | 0·223 | 0·254 | 0·260 | | | |
| German silver | ... | 0·043 | 0·049 | 0·056 | 0·059 | | | |
| Platinoid | ... | 0·042 | 0·047 | 0·058 | 0·060 | | | |
| Manganine ... | ... | 0·035 | 0·040 | 0·050 | 0·052 | 0·053 | 0·063 | |
| Lipowitz alloy | ... | 0·042 | 0·043 | 0·044 | 0·044 | | | |

The Action of Ozone on Water-colour Pigments.

By Sir WILLIAM DE W. ABNEY, K.C.B., F.R.S.

(Received November 21,—Read December 12, 1907.)

In 1888 a report* upon "The Action of Light on Water Colours" was made to the Science and Art Department by Dr. Russell and myself, in which we showed that mineral colours are far more stable than vegetable colours, that the presence of moisture and oxygen are in most cases essential for a change to be effected even in the case of vegetable colours, that every colour is permanent *in vacuo*, and that the spectrum colours which principally cause fading lie at the blue end.

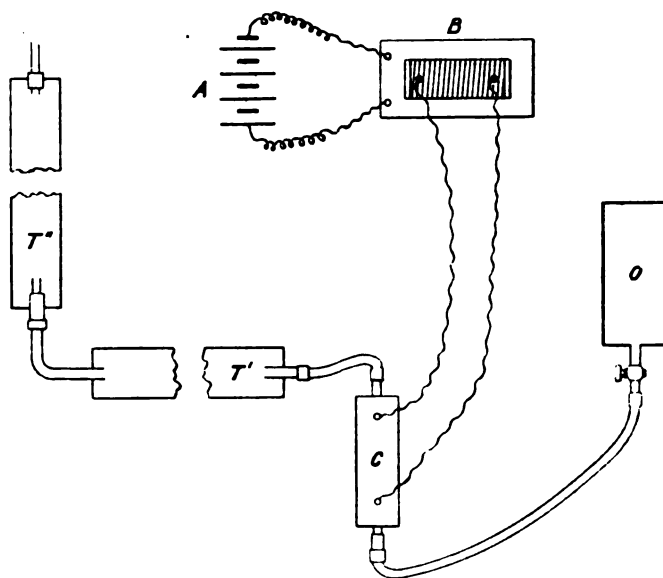
From time to time since then I have occupied myself and experimented with pigments. Amongst others, one set of experiments was made which is fairly complete, and which I wish to lay before the Royal Society, as it may prove to be a starting point for other investigations. They show that water-colour pigments (which, by the bye, are usually the same pigments as oil pigments, the only difference between the two being the vehicle in which they are situated) might fade without any assistance of light when freely exposed to the air, and it is not improbable that the action of light in some measure in the presence of the pigment produces the effective cause in the surrounding atmosphere.

It was suspected from the first, and indeed the report alluded to above implies it, that the fading of colours is due to oxidation. If such be the cause, then the introduction of an active oxidising agent such as ozone (or peroxide of hydrogen) into the atmosphere should show the same effect as the prolonged exposure to light. To ascertain if such were the case, strips of varying depths, of different single colours or of mixtures of colours, were prepared, so that the effect might be studied on well-separated particles, and also when they were closer together. In fact, strips were prepared as described in the report. A piece of apparatus was put together, as shown diagrammatically in the following figure (p. 147).

A is a four-cell Grove battery working a coil B, which is connected with C an ozone tube, to which are attached, as shown, a series of wide tubes T' and T'', in which strips of pigmented paper can be readily introduced. O is an oxygen bottle supplying the ozone tube with a slow stream of oxygen.

The various strips were well moistened at the back, so that the pigmented surface was damp.

* Subsequently printed and presented to both Houses of Parliament.



When everything was arranged, the flow of oxygen was commenced and the coil put in action. The following extract from my note-book of the first day's work will show the kind of strip and length of time required for experiments with the different colours :—

June 22.

- 11.15 Put into the tubes crimson lake, Payne's grey, Antwerp blue, and indigo. Bleaching at once began in crimson lake, Payne's grey, and indigo.
- 11.45 Took out crimson lake, quite bleached.
- 12.0 " indigo " "
- 12.15 " Payne's grey " "
- Antwerp blue unchanged.
- 1.35 Put in tubes ultramarine blue, chrome yellow, and a fresh strip of indigo.
- 1.38 Faint wash of indigo, quite bleached.
- 2.0 Next " " " "
- 2.15 Took out indigo; darkest wash gone pale green.
- 2.30 Put in tube Prussian blue.
- 3.0 Put in indigo + gamboge* (*i.e.*, a green made of these two colours), and of Prussian blue + raw sienna (*i.e.*, a green made of these two colours). Took out chrome yellow and ultramarine blue, and found no appreciable change.

* Indigo + gamboge means a green made by mixing indigo and gamboge together; the + sign always means a mixture.

- 3.20 Indigo + gamboge, indigo bleaching; light washes bleached. Gamboge, light shades quite bleached, and darker shades much lighter.
- 3.45 Indigo + gamboge, action seemingly over.
- 4.5 Indigo + Venetian red (a grey), and indigo + Indian red (a grey) put in tube. Rapid disappearance of the blue began immediately, and at
- 4.20 No trace of the indigo appears but in the darkest wash.
- 4.30 Action stopped. No further change in the indigo + Venetian red or in the indigo + Indian red. No change noticed in Prussian blue, Antwerp blue, or in Prussian blue + raw sienna.

| Colours exposed to light by Russell and Abney in moist air. | Time taken to bleach in damp ozonised air. | Composition of colour, according to Winsor and Newton. |
|---|--|---|
| <i>Unchanged.</i> | | |
| Indian red | h. m. | A variety of iron oxide. |
| Venetian red | " | Artificially prepared sesquioxide of iron. |
| Burnt sienna | " | Burnt raw sienna. |
| Yellow ochre | " | Native earth. |
| Raw sienna | " | " |
| Emerald green | 0 45 | Acetoarsenite of copper. |
| Terre verte | " | Native earth. |
| Chromium oxide | " | Chromium sesquioxide. |
| Cobalt blue | " | Alumina tintured with cobalt oxide. |
| Ultramarine ash | " | Second quality of blue from lapis lazuli. |
| Chrome yellow | " | Normal chromate of lead. |
| <i>Altered.</i> | | |
| Vermillion | " | Mercuric sulphide. |
| Rose madder | 4 0 | Lake from the madder root. |
| Brown madder | 2 10 | " |
| Gamboge | 0 50 | A gum resin. |
| Aureolin | " | Double nitrite of cobalt and potassium. |
| Cadmium yellow | 4 0 | Sulphide of cadmium. |
| Naples yellow | 0 45 | Cadmium yellow and zinc white. |
| Indian yellow | 4 0 | Prepared "purree" from India. |
| Olive green | 1 5 | Indian yellow, umber, and indigo. |
| Indigo | 0 40 | Vegetable blue from indigo plant. |
| French blue | 3 30 | Artificial ultramarine. |
| Permanent blue | 3 30 | A pure variety of French blue. |
| Payne's grey | 1 0 | Indigo, crimson lake, and carbon black. |
| Violet carmine | 4 0 | A lake obtained from the root of <i>Anchusa tinctoria</i> . |
| Purple madder | 0 20 | Lake from the madder root. |
| Sepia | 0 50 | From the cuttlefish bags. |
| Brown pink | 0 30 | Lake from quercitron bark. |
| Vandyke brown | 1 15 | Native earth. |
| <i>Destroyed.</i> | | |
| Carmine | 0 10 | Lake prepared from cochineal. |
| Crimson lake | 0 30 | " |
| Antwerp blue | " | A weak variety of Prussian blue containing alumina. |
| Prussian blue | " | Ferrocyanide of iron. |

The table on p. 148 shows the results obtained. The first column is a list of colours exposed to light in moist air *in the order of stability*. It is copied from the report above mentioned. The second column shows the time taken to bleach or change the colours in a moist atmosphere of ozone. (*u* signifies that no change took place in the colours after prolonged exposure.) The third column shows the composition of the different colours (*water colours*) according to Winsor and Newton's catalogue.

The following table shows the time of fading when certain mixtures were tested:—

| Mixtures submitted to damp ozone. | Time of fading. | Remarks. |
|-----------------------------------|-----------------|------------------|
| | Mins. | |
| Carmine + Prussian blue | 15 | Blue left. |
| " + Leitner's blue | 15 | " |
| Indigo + gamboge | 45 | Both " bleached. |
| " + Venetian red | 25 | Red left. |
| " + Indian red | 25 | " |
| " + burnt sienna | 10 | Sienna left. |
| " + Indian yellow | 10 | Blue gone. |
| " + Vandyke brown | 10 | " |
| " + yellow ochre | 10 | " |
| Crimson lake + cobalt | 30 | Cobalt left. |
| " + Antwerp blue ... | 20 | Blue left. |
| " + Prussian blue ... | 8 | " |

It will be seen that the ozone had no effect on any of the colours which light failed to affect with the single exception of emerald green. From its composition it is not strange that some effect should take place in it. Again, it will be noticed that all the colours unchanged by the ozone are mineral colours. In the list of colours destroyed by light are Prussian and Antwerp blue, both of which are of the same composition. Ozone had no effect on either of them. In the report referred to it was mentioned that if bleached Prussian blue were placed in the dark its colour revived. Presumably there is some action caused by light which is absent when the exposure is to ozone. Two other colours unchanged by ozone are aureolin and vermilion, both of which are high up in the "altered" list. In light, vermilion blackened and aureolin lost but little. In regard to the remaining colours the order of bleaching would be slightly altered. Beginning with those which took longer to bleach, we should have—

| | | | |
|-----------------|-----------------|----------------|----------------|
| Rose madder. | French blue. | Payne's Grey. | Indigo. |
| Cadmium yellow. | Permanent blue. | Gamboge. | Brown pink. |
| Indian yellow. | Vandyke brown. | Sepia. | Crimson lake. |
| Violet carmine. | Olive green. | Naples yellow. | Purple madder. |
| | Carmine. | | |

Those in the list as far as permanent blue took hours to be bleached and should be regarded as permanent so far as moist ozone is concerned. The remainder must be looked upon as fugitive, the five last being very fugitive.

Another set of experiments was carried out in which dry ozone was introduced into the tubes, the oxygen bubbling through strong sulphuric acid and passing over phosphoric anhydride before it reached the ozone tube. The pigments were dried in an oven and then placed in the tubes.

No change took place in any of the colours, though submitted to the dry ozone for a long period. As in the experiments with light, it is evident that moisture must be present in order that bleaching may take place. It is unnecessary to make any deductions from the experiments, except to point out that the life of the colours will be longer in an atmosphere free from an active oxidising agent. I have to thank Mr. C. R. Woods for the care he took in carrying out, under my direction, the various experiments.

Preliminary Note on the Operational Invariants of a Binary Quantic.

By Major P. A. MACMAHON, D.Sc., F.R.S.

(Received October 8,—Read December 12, 1907.)

My object is to present a theory of operational invariants for the binary quantic of order n . Many of the results that are here given have been explicitly or implicitly given in the works of Cayley, Clebsch, Gordan, and other writers, but not from the present point of view or in the convenient notation that will be adopted. Some quite new results are reached, which will be found to throw much light upon the work of others.

1. In the algebraic theory we take the quantic to be

$$a_x^n = (a_1x_1 + a_2x_2)^n,$$

and b, c, d, \dots as alternative symbolic letters to a . We then have symbolic factors of two types, viz., the suffix type, a_x , and the bracketed or determinant type (ab) . In fact, for the substitution

$$x_1 = \lambda_1 X_1 + \mu_1 X_2,$$

$$x_2 = \lambda_2 X_1 + \mu_2 X_2,$$

the determinant of which is

$$\lambda_1\mu_2 - \lambda_2\mu_1 = (\lambda\mu) = \Delta,$$

we have

$$a_x^n = A_x^n = (A_1X_1 + A_2X_2)^n;$$

where

$$A_1 = a_1\lambda_1 + a_2\lambda_2 = a_\lambda,$$

$$A_2 = a_1\mu_1 + a_2\mu_2 = a_\mu,$$

$$(ab) = \Delta^{-1}(AB).$$

The real form of a_x^n is

$$a_0x_1^n + \binom{n}{1}a_1x_1^{n-1}x_2 + \binom{n}{2}a_2x_1^{n-2}x_2^2 + \dots + a_nx_2^n.$$

I write symbolically

$$\partial_{a_s} = \binom{n}{s} a_1^{n-s} a_2^s,$$

$$\frac{\partial^{p+q}}{\partial x_1^p \partial x_2^q} = \xi_1^p \xi_2^q;$$

whence it is readily seen that

$$a_1, a_2$$

are cogredient to

$$x_1, x_2;$$

and that

$$\xi_1, \xi_2$$

are cogredient to

$$a_1, a_2;$$

and that thus we obtain the new invariant symbolic factors

$$(x\alpha), (\alpha\beta), (\alpha\xi), (\xi\eta).$$

$$x_{\xi}, \quad \alpha_{\xi}, \quad \alpha_{\alpha}, \quad \alpha_{\xi}.$$

To make this clear, I write the symbolic letters in two rows—

$$x, y, z, \dots, \quad \alpha, \beta, \gamma, \dots,$$

$$\alpha, b, c, \dots, \quad \xi, \eta, \zeta, \dots,$$

where $x, y, z, \dots, \alpha, \beta, \gamma, \dots, \alpha, b, c, \dots, \xi, \eta, \zeta, \dots$ are alternative letters respectively, and remark that all letters in the same row are cogredient, and that letters which are in different rows are contragredient. Determinant invariant symbolic factors are obtained from any two letters in the same row, and suffix invariant symbolic factors from any two letters in different rows.

An invariant factor corresponds to *every* pair of letters, so that if there be p different letters, there will be

$$\binom{p}{2}$$

invariant symbolic factors.

As regards any two letters in the first row, the substitution gives

$$(xy) = \Delta(XY),$$

the power of the modulus for transformation being unity.

For any two letters in the second row

$$(\alpha\xi) = \Delta^{-1}(A\xi),$$

the power of the modulus being negative unity. For any two letters in different rows the invariance is absolute, *e.g.*, $x_{\xi} = X_{\xi}$.

In a symbolic product absolute invariance is secured when the number of determinant factors drawn from the first row is equal to the number drawn from the second. The power of the modulus is always equal to the excess of the number of such factors drawn from the first row over the number drawn from the second.

We are now able to form a calculus of operational invariants. All the operational processes at present in existence, including those which produce evectants, provectants, and emanants, the Aronhold process, the Ω process, and transvection, are included in the present enlarged symbolism. An invariant operator may or may not involve the variables x_1, x_2 , and it may be separable into two portions, one of which involves the variables, while the other does not. The different classes will present themselves for examination as the work proceeds. Those operators which do not involve ξ_1 and ξ_2 may be homogeneous in the variables, and are then analogous to algebraical

covariants. The leading coefficient will then be found to have semi-invariant properties, and, of course, the same also may be said of the end coefficients.

2. First consider the covariant $(x\alpha)^n$ of the quantic α_x^n . In unsymbolic form it is

$$(\partial_{a_n}, -\partial_{a_{n-1}}, +\partial_{a_{n-2}}, \dots, \partial_{a_1}, x_2)^n,$$

or

$$x_1^n \partial_{a_n} - x_1^{n-1} x_2 \partial_{a_{n-1}} + \dots (-)^n x_2^n \partial_{a_0},$$

a covariant of order n and of degree -1 , weight $-n$ in the coefficients.

Operating upon any algebraical covariant, it produces a covariant, and it is easy to see that, in many cases, it causes the covariant to vanish. For, if the operand be of

$$(\text{deg.}, \text{weight}, \text{order}) = (i, w, \epsilon),$$

it is transformed into one of

$$(\text{deg.}, \text{weight}, \text{order}) = (i-1, w-n, \epsilon+n),$$

and vanishes for the cases

$$i = 1, w < n, w = n+1.$$

Annihilation takes place when the number of determinant factors in the operand is $n+1$ or $< n$.

In particular, α_x^n is annihilated and ($n > 2$), so is the Hessian; and so on.

In general, the symbolic factor $(x\alpha)$ is concerned with the process known as evectiou.

3. Next consider the covariant operator

$$a_x^p (x\alpha)^p \alpha_x^{n-p},$$

which is lineo-linear in the coefficients, where p may be any one of the integers $0, 1, 2, \dots, n-1$.

It has $(\text{deg.}, \text{weight}, \text{order}) = (0, -p, 2p)$,

and therefore converts any covariant of characters (i, w, ϵ) into one which has characters $(i, w-p, \epsilon+2p)$.

It is obvious that it annihilates any covariant operand for which $w < p$ or $w = p+1$. It is merely necessary to observe that the coefficient of $x_1^{\epsilon+2p}$ vanishes, and this implies the vanishing of the form. Observe also that if $i = 2$, the form vanishes unless $w-p$ is even.

The case $p = 0$ gives the single invariant operator which is lineo-linear in the coefficients, viz.,

$$\alpha_x^n = I_\alpha = a_0 \partial_{a_0} + a_1 \partial_{a_1} + \dots + a_n \partial_{a_n}.$$

In order to exhibit to the best advantage the unsymbolic forms of these operators, I write, following as far as possible the notation adopted by other writers,

$$\Omega_1 = a_0 \partial_{a_1} + 2a_1 \partial_{a_2} + \dots + na_{n-1} \partial_{a_n},$$

$$\Omega_p = a_0 \partial_{a_p} + \binom{p+1}{p} a_1 \partial_{a_{p+1}} + \binom{p+2}{p} a_2 \partial_{a_{p+2}} + \dots + \binom{n}{p} a_{n-p} \partial_{a_n},$$

$$O_1 = a_n \partial_{a_{n-1}} + 2a_{n-1} \partial_{a_{n-2}} + \dots + na_1 \partial_{a_0},$$

$$O_p = a_n \partial_{a_{n-p}} + \binom{p+1}{p} a_{n-1} \partial_{a_{n-p-1}} + \binom{p+2}{p} a_{n-2} \partial_{a_{n-p-2}} + \dots + \binom{n}{p} a_p \partial_{a_0};$$

where, to explain, if \dagger be a symbol to denote operation upon the symbols of quantity only, the differential inverses being regarded as constants,

$$\frac{1}{2!} \Omega_2 = \Omega_1 \dagger \Omega_1,$$

$$\frac{1}{3!} \Omega_3 = \Omega_1 \dagger \Omega_1 \dagger \Omega_1,$$

$$\dots \dots \dots$$

$$\frac{1}{2!} O_2 = O_1 \dagger O_1,$$

$$\frac{1}{3!} O_3 = O_1 \dagger O_1 \dagger O_1,$$

$$\dots \dots \dots$$

I further write

$$W = W_1 = a_1 \partial_{a_1} + 2a_2 \partial_{a_2} + \dots + na_n \partial_{a_n},$$

$$W_p = a_1 \partial_{a_1} + 2^p a_2 \partial_{a_2} + \dots + n^p a_n \partial_{a_n};$$

where, to explain the formation,

$$W_2 = W_1 \dagger W_1,$$

$$W_3 = W_1 \dagger W_1 \dagger W_1,$$

$$\dots \dots \dots$$

Observe that the notation gives

$$I = \Omega_0 = O_0 = W_0.$$

I further find it convenient to write symbolically

$$W_p = W^p,$$

so that

$$\frac{1}{2} (W_2 - W_1) = \binom{W}{2},$$

$$\frac{1}{6} (W_3 - 3W_2 + 2W_1) = \binom{W}{3}.$$

$$\dots \dots \dots$$

4. When $p = 1$, I find, for $a_x (\alpha x) a_x^{n-1}$, the expression

$$x_1^2 \Omega_1 - x_1 x_2 (nI - 2W) - x_2^2 O_1,$$

which merits a careful study, as it is the simplest invariantive form which involves the well-known seminvariant operators Ω_1, O_1 .

From the known properties of Ω_1 , $nI - 2W$, and O_1 it is clear that it annihilates every invariant of a_x^n .

Also Ω_1 annihilates the leading coefficient of every covariant. Hence, when a covariant ϕ_x^e is the operand, the term involving x_1^{e+2} is absent, and, as a result, the operator annihilates also every covariant of a_x^n .

Next, in the operator, put $x_1 = x_2 = 1$. We see that the sum of the coefficients of any covariant satisfies the equation

$$\Omega_1 - (nI - 2W) - O_1 = 0.$$

The isobaric solutions of this equation are invariants. The symbolic form of this operator is

$$(a_1 + a_2)(a_2 - a_1)a_x^{n-1};$$

it annihilates

$$(\phi_1 + \phi_2)^e,$$

if ϕ_x^e be any covariant.

Any covariant $\phi_x^e = (\phi_0, \phi_1, \phi_2, \dots, x_1, x_2)^e$

has the property that any three consecutive coefficients,

$$\phi_e, \phi_{e+1}, \phi_{e+2},$$

satisfy the relation

$$\Omega_1 \phi_{e+2} - (nI - 2W) \phi_{e+1} - O_1 \phi_e = 0,$$

wherein ϕ , with a negative suffix or with a suffix greater than e , is to be put equal to zero.

It will be noted that the operators Ω_1 , O_1 from their positions in the covariant are themselves seminvariants.

Next take the Hessian of the covariant operator, viz.,

$$4\Omega_1 O_1 + (nI - 2W)^2,$$

where the multiplications are purely algebraical and not at all operational.

We have thus an invariant operator of the second order, which will come under view later on in connection with Cayley's operators

$$x_2 \partial_{x_1} - \Omega_1, \quad x_1 \partial_{x_2} - O_1.$$

5. I pass to the case $p = 2$, which has the unsymbolic form

$$\begin{aligned} & x_1^4 \Omega_2 \\ & - x_1^3 x_2 \left\{ \binom{n-1}{1} I - 2W \right\} \Omega_1 \\ & + x_1^2 x_2^2 \left\{ \binom{n}{2} I - 3 \binom{n-1}{1} W + 6 \binom{W}{2} \right\} \\ & - x_1 x_2^3 O_1 \left\{ \binom{n-1}{1} I - 2W \right\} \\ & + x_2^4 O_2, \end{aligned}$$

wherein the multiplications of operators are such that the left-hand operator is performed merely upon the literal coefficients of the right-hand operator, and not at all upon the differential inverses.

$$\begin{aligned} \text{Ex.}— \quad W_1 \Omega_1 &= (a_1 \partial_{a_1} + 2a_2 \partial_{a_2} + \dots)(a_0 \partial_{a_1} + 2a_1 \partial_{a_2} + \dots) \\ &= 1 \cdot 2 a_1 \partial_{a_2} + 2 \cdot 3 a_2 \partial_{a_3} + \dots, \\ O_1 W_1 &= (a_n \partial_{a_{n-1}} + 2a_{n-1} \partial_{a_{n-2}} + \dots)(a_1 \partial_{a_1} + 2a_2 \partial_{a_2} + \dots) \\ &= 1 \cdot n - 1 \cdot a_n \partial_{a_{n-1}} + 2 \cdot n - 2 \cdot a_{n-1} \partial_{a_{n-2}} + \dots \end{aligned}$$

I note first that the operator always produces a covariant.

Ω_2 and O_2 are seminvariants. Ω_2 , for example, either annihilates a leading seminvariant or converts it into another one. In the former case the operator covariant causes the operand covariant to vanish; for

$$\Omega_2 = a_0 \partial_{a_2} + 3a_1 \partial_{a_3} + 6a_2 \partial_{a_4} + \dots,$$

and the alternant of Ω_1 and Ω_2 does in fact vanish.

What seminvariants are caused to vanish by this operator Ω_2 ? The reply to this question is supplied by the theory of symmetric functions. For make the transformation

$$a_i = s! b_i,$$

so that the seminvariants are non-unitary symmetric functions of the roots of the equation

$$b_0 x^m - b_1 x^{m-1} + b_2 x^{m-2} - \dots = 0;$$

$$\Omega_2 \text{ is equivalent to } b_0 \partial_{b_2} + b_1 \partial_{b_3} + b_2 \partial_{b_4} + \dots,$$

and this again to

$$D_1^2 - 2D_2,$$

$$\text{where } D_\kappa = \frac{1}{\kappa!} (b_0 \partial_{b_1} + b_1 \partial_{b_2} + b_2 \partial_{b_3} + \dots)^\kappa.$$

Take a non-unitary symmetric function—

$$\Sigma \alpha^{k_1} \beta^{k_2} \gamma^{k_3} \dots = (k_1 k_2 k_3 \dots);$$

then

$$D_{k_1} (k_1 k_2 k_3 \dots) = (k_2 k_3 \dots),$$

and D_k annihilates every symmetric function whose partition contains no part k .

Hence Ω_2 here is equivalent to D_2 and all symmetric functions which, when expressed in partitions, contain no part 2 are solutions of the equation

$$\Omega_2 = 0.$$

$$\text{E.g., the covariant } (a_0^2 a_3 - 3a_0 a_1 a_2 + 2a_1^3) x_1^5 + \dots$$

is annihilated by the quantic covariant operator, because $a_0^2 a_3 - 3a_0 a_1 a_2 + 2a_1^3$, when transformed, is the symmetric function $\Sigma \alpha^3$ or (3), the number 2 not appearing in the partition. The covariant of deg. 3 and weight 5 in the

coefficient is not annihilated because the corresponding partition is (32); we learn, moreover, that the result of the operation is the covariant of deg. weight (3, 3) which corresponds to the partition (3).

Generally the covariant $(ab)^2 a_x^2 b_x^2$
is converted into $(ab)^{2s-2} a_x^{s+2} b_x^{s+2}$.

The operator, for the quantic, is, on development,

$$\begin{aligned} & x_1^4 (a_0 \partial_{a_1} + 3a_1 \partial_{a_2} + 6a_2 \partial_{a_3}) \\ & - x_1^3 x_2 (3a_0 \partial_{a_1} + 2a_1 \partial_{a_2} - 3a_2 \partial_{a_3} - 12a_3 \partial_{a_4}) \\ & + 3x_1^2 x_2^2 (2a_0 \partial_{a_0} - a_1 \partial_{a_1} - 2a_2 \partial_{a_2} - a_3 \partial_{a_3} + 2a_4 \partial_{a_4}) \\ & - x_1 x_2^3 (-3a_4 \partial_{a_3} - 2a_3 \partial_{a_2} + 3a_2 \partial_{a_1} + 12a_1 \partial_{a_0}) \\ & + x_2^4 (a_4 \partial_{a_1} + 3a_3 \partial_{a_2} + 6a_2 \partial_{a_3}), \end{aligned}$$

of which the symmetry does not escape attention.

6. When $p = 3$ we obtain an annihilator, which has the form

$$\begin{aligned} & x_1^6 \Omega_3 \\ & - x_1^5 x_2 \left\{ \binom{n-2}{1} I - 2W \right\} \Omega_2 \\ & + x_1^4 x_2^2 \left\{ \binom{n-1}{2} I - \frac{5}{2} \binom{n-2}{1} W + 5 \binom{W}{2} \right\} \Omega_1 \\ & - x_1^3 x_2^3 \left\{ \binom{n}{3} I - 4 \binom{n-1}{2} W + 10 \binom{n-2}{1} \binom{W}{2} - 20 \binom{W}{3} \right\} \\ & - x_1^2 x_2^4 O_1 \left\{ \binom{n-1}{2} I - \frac{5}{2} \binom{n-2}{1} W + 5 \binom{W}{2} \right\} \\ & + x_1 x_2^5 O_2 \left\{ \binom{n-2}{1} I - 2W \right\} \\ & - x_2^6 O_3, \end{aligned}$$

operative for all quantics of order not less than 4.

7. The unsymbolic form of the operator

$$a_x^p (x\alpha)^p a_x^{n-p}$$

is

$$\begin{aligned} & x_1^{2p} \Omega_p \\ & - x_1^{2p-1} x_2 \left\{ \binom{n-p+1}{1} I - \frac{\binom{2p}{1}}{\binom{p}{1}} W \right\} \Omega_{p-1} \\ & + x_1^{2p-2} x_2^2 \left\{ \binom{n-p+2}{2} I - \frac{\binom{2p-1}{1}}{\binom{p-1}{1}} \binom{n-p+1}{1} W + \frac{\binom{2p}{2}}{\binom{p}{2}} \binom{W}{2} \right\} \Omega_{p-2} \\ & + \dots \end{aligned}$$

$$\begin{aligned}
& + (-)^s x_1^{2p-s} x_2^s \left\{ \binom{n-p+s}{s} I - \frac{\binom{2p-s+1}{1}}{\binom{p-s+1}{1}} \binom{n-p+s-1}{s-1} W \right. \\
& \quad \left. + \frac{\binom{2p-s+2}{2}}{\binom{p-s+2}{2}} \binom{n-p+s-2}{s-2} \binom{W}{2} - \dots + (-)^s \frac{\binom{2p}{s}}{\binom{p}{s}} \binom{W}{s} \right\} \Omega_{p-s} \\
& + \dots \\
& + (-)^p x_1^p x_2^p \left\{ \binom{n}{p} I - \frac{\binom{p+1}{1}}{\binom{1}{1}} \binom{n-1}{p-1} W + \frac{\binom{p+2}{2}}{\binom{2}{2}} \binom{n-2}{p-2} \binom{W}{2} - \dots \right. \\
& \quad \left. + (-)^p \binom{2p}{p} \binom{W}{p} \right\} \\
& + \dots \\
& + (-)^{p+s} x_1^s x_2^{2p-s} O_{p-s} \left\{ \binom{n-p+s}{s} I - \frac{\binom{2p-s+1}{1}}{\binom{p-s+1}{1}} \binom{n-p+s-1}{s-1} W \right. \\
& \quad \left. + \frac{\binom{2p-s+2}{2}}{\binom{p-s+2}{2}} \binom{n-p+s-2}{s-2} \binom{W}{2} - \dots + (-)^s \frac{\binom{2p}{s}}{\binom{p}{s}} \binom{W}{s} \right\} \\
& + \dots \\
& + (-)^p x_1^2 x_2^{2p-2} O_{p-2} \left\{ \binom{n-p+2}{2} I - \frac{\binom{2p-1}{1}}{\binom{p-1}{1}} \binom{n-p+1}{1} W + \frac{\binom{2p}{2}}{\binom{p}{2}} \binom{W}{2} \right\} \\
& + (-)^{p+1} x_1 x_2^{2p-1} O_{p-1} \left\{ \binom{n-p+1}{1} I - \frac{\binom{2p}{1}}{\binom{p}{1}} W \right\} \\
& + (-)^p x_2^{2p} O_p
\end{aligned}$$

It will be observed that, reading the rows down the page, the signs are alternately positive and negative as far as the middle row (involving $x_1^p x_2^p$) inclusive; after that row the signs are alternately negative and positive until the last row, which thus has the sign $(-)^p$.

It is operative for all quantics of order not less than $p+1$.

The Operators

$$\begin{aligned}
x_2 \partial_{x_1} &= \Omega_1, \\
x_1 \partial_{x_2} &= O_1.
\end{aligned}$$

8. Cayley, in his introductory memoir upon Quantics, defined a covariant of

a_x^n as a form which is annihilated by each of these operators. By the linear transformation are obtained the formulæ

$$\begin{aligned}\Delta(x_2\xi_1 - \Omega_a) &= \mu_2^2(X_2\Xi_1 - \Omega_A) \\ &\quad + \lambda_2\mu_2\{X_1\Xi_1 - X_2\Xi_2 - (nI_A - 2W_A)\} \\ &\quad - \lambda_2^2(X_1\Xi_2 - O_A),\end{aligned}$$

$$\begin{aligned}\Delta\{x_1\xi_1 - x_2\xi_2 - (nI_a - 2W_a)\} &= 2\mu_1\mu_2(X_2\Xi_1 - \Omega_A) \\ &\quad + (\lambda_1\mu_2 + \lambda_2\mu_1)\{X_1\Xi_1 - X_2\Xi_2 - (nI_A - 2W_A)\} \\ &\quad - 2\lambda_1\lambda_2(X_1\Xi_2 - O_A),\end{aligned}$$

$$\begin{aligned}\Delta(x_1\xi_2 - O_a) &= -\mu_1^2(X_2\Xi_1 - \Omega_A) \\ &\quad - \lambda_1\mu_1\{X_1\Xi_1 - X_2\Xi_2 - (nI_A - 2W_A)\} \\ &\quad + \lambda_1^2(X_1\Xi_2 - O_A),\end{aligned}$$

from which it is clear that a third annihilator of all covariants, viz.,

$$x_1\partial_{x_1} - x_2\partial_{x_2} - (nI - 2W),$$

should be added to the two of Cayley.

We derive at once the absolute invariant

$$4(x_2\xi_1 - \Omega_1)(x_1\xi_2 - O_1) + \{x_1\xi_1 - x_2\xi_2 - (nI - 2W)\}^2,$$

wherein the multiplications are algebraical and not at all operational.

The symbolic form of this invariant is

$$x_\xi^2 + 2na_\alpha^n x_\xi - n^2 a_\alpha^n b_\beta^n - 4na_\alpha^{n-1} a_x x_\xi + 2n^2 a_\alpha^{n-1} b_\beta^{n-1} a_\beta b_\alpha;$$

where observe that the absence of determinant factors shows that it is absolute.

Observe also that we have already obtained the absolute invariant

$$4\Omega_1 O_1 + (nI - 2W)^2,$$

whose symbolic form is $n^2 a_\alpha^{n-1} b_\beta^{n-1} (2a_\beta b_\alpha - a_\alpha b_\beta)$.

This was obtained as the discriminant of the quadratic covariant

$$\begin{aligned}x_1^2 \Omega_1 - x_1 x_2 (nI - 2W) - x_2^2 O_1 \\ \equiv a_x (x_\alpha) a_\alpha^{n-1}.\end{aligned}$$

It might also have been obtained by taking the y -discriminant of the second polar of this covariant—

$$\begin{aligned}y_1^2 \Omega_1 - y_1 y_2 (nI - 2W) - y_2^2 O_1 \\ \equiv a_y (y_\alpha) a_\alpha^{n-1},\end{aligned}$$

and since the invariantive form

$$-(xy) y_\xi - a_y (y_\alpha) a_\alpha^{n-1}$$

has the unsymbolic expression

$$y_1^2 (x_2\xi_1 - \Omega_1) - y_1 y_2 \{x_1\xi_1 - x_2\xi_2 - (nI - 2W)\} - y_2^2 (x_1\xi_2 - O_1),$$

we find the covariant under examination by taking its discriminant.

The Operator $(a\xi)^{\pi}a_x^{n-\pi}$.

9. This is of degree one and weight zero in the coefficients and of order $n-2\pi$ in the variables; and p may be any of the integers 1, 2, 3, ... n .

Writing $a_x^n = f$, when $\pi = 1$,

$$n(a\xi)a_x^{n-1} = \frac{df}{dx_1}\xi_2 - \frac{df}{dx_2}\xi_1;$$

and, the operand being any covariant $\phi_x^n = \phi$, we obtain

$$\frac{df}{dx_1}\frac{d\phi}{dx_2} - \frac{df}{dx_2}\frac{d\phi}{dx_1},$$

which is the Jacobian of f and ϕ .

Similarly, if ϕ and ψ be any two covariants of orders p and q in the variables, the operation of

$$p(\phi\xi)\phi_x^{p-1} \text{ upon } \psi_x^q$$

produces the Jacobian of ϕ and ψ , viz.,

$$\frac{d\phi}{dx_1}\frac{d\psi}{dx_2} - \frac{d\phi}{dx_2}\frac{d\psi}{dx_1};$$

and the operation of

$$q(\psi\xi)\psi_x^{q-1} \text{ upon } \phi_x^p$$

produces

$$\frac{d\psi}{dx_1}\frac{d\phi}{dx_2} - \frac{d\psi}{dx_2}\frac{d\phi}{dx_1};$$

viz., the same Jacobian with negative sign.

In other words, the first transvectant (überschiebung) of ϕ over ψ is obtained by the operation of

$$p(\phi\xi)\phi_x^{p-1} \text{ upon } \psi_x^q,$$

and interchange of the forms ϕ , ψ merely changes the sign of the result.

We may write the theorem in the form

$$\begin{aligned} & p(\phi\xi)\phi_x^{p-1} \cdot \psi_x^q \\ &= -q(\psi\xi)\psi_x^{q-1} \cdot \phi_x^p \\ &= pq(\phi\psi)\phi_x^{p-1} \cdot \psi_x^{q-1}. \end{aligned}$$

Passing to the case $\pi = 2$, we find

$$\begin{aligned} & n(n-1)(a\xi)^2 a_x^{n-2} \\ &= \frac{d^2 f}{dx_1^2} \xi_2^2 - 2 \frac{d^2 f}{dx_1 dx_2} \xi_1 \xi_2 + \frac{d^2 f}{dx_2^2} \xi_1^2; \end{aligned}$$

and thus, if ϕ_x^p , ψ_x^q be any two covariants,

$$\begin{aligned} & p(p-1)(\phi\xi)^2 \phi_x^{p-2} \cdot \psi_x^q \\ &= \frac{d^2 \phi}{dx_1^2} \cdot \frac{d^2 \psi}{dx_2^2} - 2 \frac{d^2 \phi}{dx_1 dx_2} \cdot \frac{d^2 \psi}{dx_1 dx_2} + \frac{d^2 \phi}{dx_2^2} \cdot \frac{d^2 \psi}{dx_1^2}, \\ &= p(p-1)q(q-1)(\phi\psi)^2 \phi_x^{p-2} \psi_x^{q-2}, \end{aligned}$$

the second transvectant of ϕ over ψ .

In general, it is clear that

$$\begin{aligned} & \frac{p!}{\pi!} (\phi\xi)^\pi \phi_x^{p-\pi} \cdot \psi_x^q \\ &= (-)^\pi \frac{q!}{\pi!} (\psi\xi)^\pi \psi_x^{q-\pi} \cdot \phi_x^p, \\ &= \frac{p!}{\pi!} \frac{q!}{\pi!} (\phi\psi)^\pi \phi_x^{p-\pi} \psi_x^{q-\pi}; \end{aligned}$$

or, as it may be otherwise written,

$$\begin{aligned} & \frac{\pi!}{q!} (\phi\xi)^\pi \phi_x^{p-\pi} \cdot \psi_x^q, \\ &= (-)^\pi \frac{\pi!}{p!} (\psi\xi)^\pi \psi_x^{q-\pi} \cdot \phi_x^p, \\ &= (\phi\psi)^\pi \phi_x^{p-\pi} \psi_x^{q-\pi}; \end{aligned}$$

showing that the π th transvectant of two forms is obtainable by a pure operation upon either of the forms.

So far as the writer is aware, such a transvection has not hitherto been exhibited as the result of a pure operation. The importance of the operational invariant

$$(\alpha\xi)^\pi a_x^{n-\pi}$$

is thus evident.

The Absorption Spectra of the Vapours of Benzene and its Homologues at Different Temperatures and Pressures, and likewise of Solutions of Benzene.

By WALTER NOEL HARTLEY, F.R.S., D.Sc., Royal College of Science, Dublin.

(Received August 15,—Read December 12, 1907.)

(Abstract.)

The author having been engaged since the year 1877 in investigating and correlating the physical and chemical properties of aromatic substances in relation to their chemical structure or constitution, he has latterly found it desirable that several very definite compounds should be examined in a state of vapour, as well as in solution.

The work of E. Pauer,* W. Friederichs,† and of L. Grebe‡ is referred to in detail. The vapours of benzene and several of its derivatives have been examined (1) at different temperatures and constant pressure; and (2) at different pressures, the temperature being constant. The previous measurements of Pauer, Friederichs, and Grebe have been confirmed, and reconciled where they do not show complete agreement with each other. The records of temperature and pressure, and the shortening of the exposure of the photographic plates, constitute important differences between the work of the former investigators and that of the author.

Details of the following photographs are given :—

Absorption Bands in the Spectrum of Benzene Vapour at Different Temperatures and a Barometric Pressure of 755·5 mm.

| | | | | |
|---|-------|-----|-----|-----|
| Temperatures | 12°·5 | 25° | 43° | 53° |
| Number of bands photographed and measured | 55 | 84 | 82 | 56 |

Absorption Bands in the Spectrum of Benzene Vapour at 11°·5 and Different Pressures.

| | | | | |
|--------------------------------|-----|-----|-----|----|
| Pressures in millimetres | 778 | 483 | 253 | 21 |
| Number of bands measured..... | 36 | 38 | 46 | 44 |

The same at 100° and Different Pressures.

| | | | | | | |
|--------------------------------|-----|-----|-----|-----|-----|-----|
| Pressures in millimetres..... | 683 | 589 | 478 | 381 | 279 | 172 |
| Number of bands measured | 9 | 13 | 14 | 16 | 17 | 18 |

The same at 100°.

| | | | | | | | | |
|-------------------------------|-----|-----|-----|-----|-----|-----|----|----|
| Pressures in millimetres..... | 767 | 591 | 484 | 332 | 206 | 142 | 99 | 88 |
| Number of bands measured | 5 | 9 | 9 | 12 | 13 | 11 | 14 | 15 |

The same at 100°.

| | | | |
|--------------------------------|----|----|----|
| Pressures in millimetres..... | 92 | 69 | 43 |
| Number of bands measured | 25 | 36 | 50 |

* 'Annalen,' 1897, vol. 61, p. 363.

† 'Zeitschr. f. Wissenschaftliche Photographie,' 1905, p. 633.

‡ *Loc. cit.*, 1905, p. 363.

The Absorption Spectra of the Vapours of Benzene, etc. 163

| | | | | | | | | | |
|-------------------------------|------|------|------|------|------|------|----|----|----|
| The same at 100°. | | | | | | | | | |
| Pressures in millimetres..... | 67·5 | 52·5 | 37·5 | 28·5 | 22·5 | 15·5 | 9 | 5 | 4 |
| Number of bands measured | 31 | 54 | 60 | 72 | 75 | 88 | 52 | 38 | 30 |

Absorption Bands in the Spectrum of Toluene Vapour at Different Temperatures and Constant Pressure.

| | | | | | | | | | |
|--------------------------|-----|-----|-----|-----|-----|-----|-----|-----|------|
| Temperatures..... | 10° | 30° | 40° | 50° | 60° | 70° | 80° | 90° | 100° |
| Number of bands measured | 16 | 20 | 16 | 20 | 23 | 21 | 24 | 23 | 18 |

The Absorption Spectrum of Toluene Vapour at Different Pressures and Constant Temperature.

| | | | | | |
|--------------------------------|-----|-----|-----|-----|----|
| Pressures in millimetres..... | 763 | 563 | 371 | 174 | 43 |
| Number of bands measured | 18 | 16 | 18 | 15 | 15 |

The Absorption Bands of Ethylbenzene Vapour at Different Temperatures.

| | | | | |
|-----------------------------|-------|-----|-----|------|
| Temperatures..... | 18°·5 | 40° | 70° | 100° |
| Number of bands measured... | 19 | 18 | 8 | 2 |

General absorption
occurs here.

The same.

| | | | | | |
|-----------------------------|-----|-----|-----|-----|----------------------|
| Temperatures..... | 20° | 36° | 52° | 71° | 100° |
| Number of bands measured... | 17 | 15 | 5 | 3 | Complete absorption. |

The Absorption Bands of *o*-Xylene Vapour at Different Temperatures.

| | | | | | |
|-------------------------------|-----|-----|-------------------------------|------|------|
| Temperatures | 20° | 45° | 72° | 100° | 121° |
| Number of bands measured..... | 23 | 21 | No bands, general absorption. | | |

Absorption Bands of *m*-Xylene Vapour at Different Temperatures.

| | | | | |
|-------------------------------|-----|-----|-----|------|
| Temperatures | 11° | 40° | 70° | 100° |
| Number of bands measured..... | 26 | 41 | 6 | 5 |

General absorption occurs
between 2652 and 2429.

The same, *p*-Xylene Vapour.

| | | | | |
|--------------------------|-----|-----|-----|------|
| Temperatures..... | 10° | 40° | 70° | 100° |
| Number of bands measured | 30 | 25 | 5 | 7 |

General absorption from
2790 to 2416.

The same, Cymene Vapour.

| | | | | |
|--------------------------|-------|-----|-----|------|
| Temperatures..... | 17°·5 | 40° | 70° | 100° |
| Number of bands measured | 0 | 7 | 9 | 9 |

The same, Mesitylene Vapour.

| | | | | | | |
|--------------------------|-------|-----|-----|------|---------------------|------|
| Temperatures | 18°·5 | 45° | 72° | 100° | 120° | 140° |
| Number of bands measured | 2 | 2 | 2 | 2 | General absorption. | |

The measurements are given of similar groups of bands which occur in the vapour-spectra of benzene, toluene, ethyl benzene, and the three isomeric xylenes; benzene and toluene being compared at ordinary temperatures and also at 30° below their respective boiling points. A tabulated statement is also made of the heads of strong bands which appear to be common to benzene and its homologues. The intensities of the bands in the benzene vapour-spectrum at 100°, and different pressures, were compared with those at temperatures below its boiling point, and it was seen that the bands at

100° are almost identical with those at lower temperatures, but with this difference, that, at lower temperatures, some of the bands at the less refrangible end of the spectrum are feeble and less well defined. The vapour-spectrum of benzene is divided into groups of bands which are caused by the overlapping of two or more similarly constituted spectra differing in intensity. The strong bands number 54, there being 27 in each of two spectra. In addition, there are 30 feeble bands, which also fall into two series of similar groupings, but with less regularity. The entire number of bands observed between 12°·7 and 25°, under a pressure of 759·5 mm., are thus resolved into four spectra, of which two are composed of strong and two of weak bands.

Summary and Conclusions.

As regards the vapour-spectra, it is proved that benzene at 100° C. has the same molecular mass as at 25° or 12°·7.

The absorption bands at 100° are almost identical with those at lower temperatures, with variations as to definition in the less refrangible rays. The important influence of the position of the substituted hydrogens in benzene, upon the number and position of the bands in the spectra of its homologues, is clearly demonstrated.

Variations in the spectra of benzene at different temperatures and pressures are explained by the fact that there are two different kinds of absorption which are sharply defined and may be differentiated. First, there is the general absorption, which is broadened and extended towards the less refrangible rays by rise of temperature; secondly, there is the selective absorption, which includes all the narrow individual bands and groups of bands; they are not widened and displaced by rise of temperature, and such changes of this nature that they undergo are the effect of the overlying general absorption. The selective absorption is best studied by raising the general absorption to a maximum (at 100°), and studying the spectra produced by reduction of pressure. In this manner, any changes due to general absorption are eliminated. From the fact that increased sharpness and definition of the narrow bands is easily produced by rise of temperature, and also by reduction of pressure, the general absorption is clearly shown to be caused by encounters between the molecules, and the numerous narrow bands are to be ascribed to the vibrations of the atoms or atom-complexes within the molecules. This confirms the conclusion drawn from the study of solution-spectra published in 1881,* in 1882,† and 1885.‡

* 'J. Chem. Soc.,' vol. 39, pp. 153—165.

† *Loc. cit.*, vol. 47, pp. 685—757.

‡ 'Phil. Mag.,' 1885, vol. 19, 5th ser., p. 35.

The similar groups of bands occurring in benzene and toluene, and the close similarity between the spectra of toluene and ethylbenzene, with the further resemblance between *m*-xylene and toluene and ethylbenzene, is evidence that the mode of vibration within the benzene nucleus or ring-structure is in a great measure unaffected by the side-chain substitution.

A distinction is drawn between the absorption spectra of vapours, called *vapour-spectra*, and of solutions, called *solution-spectra*, and the relationship of one to the other is explained. Previous investigations carried on by the author for many years are briefly referred to, and it is shown how the views entertained have been confirmed by the investigation of the *vapour-spectra*. Attention is drawn to the insufficiency of ordinary chemical formulæ to represent the constitution of organic compounds, particularly of those like benzene which are of an endothermic character, since they do not take into account the distribution of energy in the molecule, and this obscures the view of the physical character of chemical structure or constitution. In short, whereas bonds and linkings in the formulæ usually written belong to a conception of chemical structure which is statical, the molecular constitution of such substances as are under discussion, when based upon the evidence derived from their optical properties, is essentially dynamical.* The relation of *solution-spectra* to *vapour-spectra* is shown, by reference to the results obtained by Pauer, Hartley and Dobbie, and by Grebe. The view entertained by Baly and Collie† that benzene has seven and no more than seven *solution-bands*, indicative of a definite making and breaking of a double linkage of the carbon atoms in the ring, has been carefully examined, and the author finds this to be incompatible with well-ascertained facts. From the measurements and numerical relations of the wave-lengths of bands in *solution-* and *vapour-spectra* it is explained how four, six, seven, eight, or nine bands may be recognised in *solution-spectra*, six of which are similarly constituted, and four of these are not only similarly constituted but very nearly of equal width, intensity, and persistency, that is to say, they have the same coefficient of extinction, and in all other respects an almost exact similarity. They correspond with four groups of *vapour-bands* which are formed by the four different series of bands which overlap, and they occur where they overlap to the greatest extent.

* "Single, double, or treble linkings are simply an incomplete method of representing the relation of the carbon-atoms to each other at some particular phase of their vibrations" ('*Phil. Mag.*,' 1885, vol. 19, pp. 55—57).

† '*Chem. Soc. Trans.*,' 1905, vol. 87, p. 1332.

*Further Consideration of the Stability of the Pear-shaped Figure
of a Rotating Mass of Liquid.*

By Sir G. H. DARWIN, K.C.B., F.R.S., Plumian Professor of Astronomy, and
Fellow of Trinity College, Cambridge.

(Received October 29,—Read December 12, 1907.)

(Abstract.)

In vol. 17, No. 3 (1905), of the 'Memoirs of the Imperial Academy of St. Petersburg,' M. Liapounoff has published an abstract of his work on figures of equilibrium of rotating liquid under the title "Sur un Problème de Tehebychef." In this paper he explains how he has obtained a rigorous solution for the figure and stability of the pear-shaped figure, and he pronounces it to be unstable. In my paper in the 'Philosophical Transactions' * I had arrived at an opposite conclusion.

The stability or instability depends, in fact, on whether the sign of a certain function, which M. Liapounoff calls A , is negative or positive.

M. Liapounoff tells us that, after having seen my conclusion, he repeated all his computations and confirmed his former result. He attributes the disagreement between us to the fact that I have only computed portion of an infinite series, and only used approximate forms for the elliptic integrals involved in the several terms. He believes that the inclusion of the neglected residue of the infinite series would lead to an opposite conclusion.

In my computation the critical function is decisively negative, whilst M. Liapounoff is equally clear that it is positive. The inclusion of the neglected residue of the series, which forms part of the function, undoubtedly tends to make the whole function positive, but after making the revision, explained in the present paper, it remains incredible, to me at least, that the neglected residue should amount to the total needed to invert the sign.

The analysis of my former investigation has been carefully re-examined throughout, and I have, besides, applied the same method to the investigation of Maclaurin's spheroid, where the solution can be verified by the known exact result.†

As a further check, the formulæ of the former paper have been examined on the hypothesis that the ellipsoid of reference reduces to a sphere. The

* A, Vol. 200, pp. 251—314.

† 'Amer. Math. Soc. Trans.,' 1903, vol. 4, p. 113, on "The Approximate Determination of the Form of Maclaurin's Spheroid," and a further note on the same subject, recently sent to the same society.

several terms correctly reproduce the analogous terms in the paper on Maclaurin's spheroid.

Dissent from so distinguished a mathematician as M. Liapounoff is not to be undertaken lightly, and I have, as explained, taken especial pains to insure correctness

Having made my revision, and completed the computations, I feel a conviction that the source of our disagreement will be found in some matter of principle, and not in the neglected residue of this series. I can now only express a hope that someone else will take up the question.

In the revision of the computations, the methods now used are much better than the old ones. In as far as this paper is a mere repetition of the former work with improved methods, the results are only stated in outline, but I now show how any of the ellipsoidal harmonic functions may be computed without approximation, and also how the functions of the second kind may be found rigorously.

The Cambridge University Press is engaged in bringing out a collection of my mathematical papers, and when we come to the paper on the "Stability of the Pear-shaped Figure," the new methods of computation will be substituted for the old.

On Kinetic Stability.

By HORACE LAMB, F.R.S.

(Received November 21,—Read December 12,—Revised December 19, 1907.)

1. The object of this paper is to illustrate the theory of kinetic stability, so far as such a theory can be said to exist, by a few simple examples. As the theory itself appears to be by no means widely known, some preliminary recapitulation seems advisable.

The difficulty of framing a definition of kinetic stability which shall be comprehensive and at the same time conform to natural prepossessions has long been recognised.* Thus, according to one definition which has been proposed, the vertical fall of a particle under gravity would be unstable; according to another the revolution of a particle in a circular orbit about a centre of force varying inversely as the cube of the distance would be reckoned as stable, although the slightest disturbance would cause the particle either to fall ultimately into the centre, or to recede to infinity, after describing in either case a spiral path with an infinite number of convolutions.

There are, however, certain restricted classes of cases where a natural definition of stability is possible and the corresponding criterion can be formulated. Suppose, in the first place, that we have a dynamical system which is the seat of cyclic motions whose *momenta* (in the generalised sense) are constant.† Apart from the cyclic motions the configuration depends on a certain number of “palpable” co-ordinates q_1, q_2, \dots, q_n , and an “equilibrium” configuration is one in which these co-ordinates can remain constant when the system is left to itself. Such an equilibrium configuration is said to be stable when the extreme variations of these co-ordinates, consequent on an arbitrary disturbance, are confined within limits which diminish indefinitely with the energy of the disturbance. Any arrangement of frictionless gyrostats gives a system of this kind; on a larger scale we have the problem of the free rotation of a liquid mass under its own gravitation.

In a second class of cases we have (again) certain co-ordinates whose values do not affect the kinetic or the potential energy, and the corre-

* Cf. F. Klein u. A. Sommerfeld, ‘Ueber die Theorie des Kreisel,’ Leipzig, 1898, ..., p. 342.

† Cf. Thomson and Tait, ‘Natural Philosophy,’ § 319, example (G); Lamb, ‘Hydrodynamics,’ 1906, §§ 140, 141.

sponding *velocities* are now supposed to be maintained constant by the application of suitable forces.* We have then to investigate the stability (in the same sense as before) of an "equilibrium" configuration in which the remaining co-ordinates q_1, q_2, \dots, q_n have constant values. As an example, the system may be attached to a rigid body which rotates with constant speed. The theory of the stability of an ocean covering a rotating globe also comes under this class.†

It has been customary, in treatises on dynamics, to discuss all such questions by the classical method of "small oscillations." If the variations of the co-ordinates q_1, q_2, \dots, q_n be regarded as infinitely small, the solution of the equations of disturbed motion is obtained in the form

$$\delta q_r = \sum C e^{\pm \lambda t}, \quad (1)$$

the values of λ^2 being determined by an algebraical or (in the case of an infinite number of degrees of freedom) a transcendental equation. If these values of λ^2 are found to be all real and negative, the undisturbed configuration is reckoned as stable, whilst if any of them are positive or complex, it is accounted as unstable. As familiar instances of problems discussed from this standpoint, we have the stability of the conical pendulum, of the steady precessional motion of a top, and so on. The general theory of the method, including the conditions of stability (in this sense), has been investigated by Routh.‡

M. Poincaré§ has, however, insisted on the fact that this method may, from a practical point of view, be altogether misleading as to the ultimate behaviour of the system. If deviations from the equilibrium configuration be resisted (as in practice they always are) by forces of a viscous character affecting the co-ordinates q_1, q_2, \dots, q_n , then in the case of absolute (statical) equilibrium the usual criterion of stability, viz., that the potential energy must be a minimum, is not affected. But in such cases of kinetic equilibrium as have been referred to, it may happen that the effect of the viscous forces is gradually to *increase* the deviation, even although the equilibrium configuration is *prima facie* (i.e., from the "classical" standpoint) thoroughly stable. A distinction is accordingly drawn between "ordinary" or "temporary" stability, i.e., stability as judged by the method of small oscillations, and "secular" or "permanent" stability, i.e., stability when regard is had to possible viscous forces affecting the co-ordinates

* Thomson and Tait, § 319, example (F).

† 'Hydrodynamics,' 1906, §§ 202, 203, 204.

‡ 'Stability of Motion,' 1877; 'Advanced Rigid Dynamics, 6th ed., 1905, chap. vi.

§ "Sur l'Equilibre d'une Masse Fluide animée d'un Mouvement de Rotation," 'Acta Math.,' 1885, vol. 7, p. 259.

q_1, q_2, \dots, q_n . The question of permanent stability is, of course, the important one in physical and cosmical applications.

Fortunately, the criteria of permanent stability are much simpler than the elaborate criteria of temporary stability investigated by Routh. In the former class of problems (that of constant cyclic momenta), the condition is that a certain function $V+K$ should be a minimum, where V is the potential energy, and K denotes the kinetic energy of the cyclic motions alone. In the second class of cases (where certain velocities are maintained constant), the condition is that the "kinetic potential" $V-T_0$ should be a minimum; here T_0 denotes the kinetic energy of the system when at "rest" in any prescribed configuration (q_1, q_2, \dots, q_n).*

These principles were clearly laid down by Poincaré in 1885, and applied to the problem of rotating fluid; but it is doubtful whether they have received adequate recognition beyond the necessarily somewhat narrow circle of writers who have been concerned with the special question.† It is for this reason only that I venture to call attention to a few practical exemplifications of the theory. These relate to the second class of cases above referred to, and in particular to the question of stability of equilibrium relative to a rigid body which is maintained in constant rotation about a fixed axis.

2. The trivial character of the first example may be excused on the ground that it shows almost intuitively the necessity for some qualification to the doctrine of "ordinary" stability. We consider a particle movable on the inner surface of a spherical bowl which rotates with constant angular velocity (ω) about the vertical diameter. If the bowl be smooth the equilibrium of the particle when in the lowest position is "ordinarily" stable, since the rotation of the bowl is quite irrelevant. But if we admit the existence of friction, however slight, between the particle and the bowl, the lowest position is "permanently" stable only so long as $\omega < \sqrt{g/a}$, where a is the radius. This results immediately from the consideration of the formula for the kinetic potential,

$$V - T_0 = -Mga \cos \theta - \frac{1}{2} M \omega^2 a^2 \sin^2 \theta, \quad (2)$$

where M is the mass of the particle, and θ is its angular distance from the lowest point. When the above value of ω is exceeded, the only permanently stable position is that in which

$$\cos \theta = \frac{g}{\omega^2 a}, \quad (3)$$

* See Poincaré, *loc. cit.*, or the author's 'Hydrodynamics,' *ll. cit.*

† The latest edition (1905) of Routh's 'Advanced Rigid Dynamics' contains no reference to the matter.

when the particle rotates with the bowl like the bob of a conical pendulum. To examine in detail the initial stage when the particle is slightly disturbed from its lowest position we may (for mathematical convenience) adopt the hypothesis of a frictional force varying as the relative velocity. If we employ horizontal rectangular axes Ox , Oy passing through the lowest point, and rotating with the bowl, we have, when x , y are small,

$$\left. \begin{aligned} \ddot{x} - 2\omega\dot{y} - \omega^2x &= -k\dot{x} - \frac{gx}{a}, \\ \ddot{y} + 2\omega\dot{x} - \omega^2y &= -k\dot{y} - \frac{gy}{a}, \end{aligned} \right\} \quad (4)$$

where k is the frictional coefficient. These equations may be combined into

$$\ddot{\zeta} + (2i\omega + k)\dot{\zeta} + \left(\frac{g}{a} - \omega^2\right)\zeta = 0, \quad (5)$$

where $\zeta = x + iy$. If we assume

$$\zeta = Ce^{\lambda t}, \quad (6)$$

$$\text{we find } \lambda = -i\omega \pm i\sqrt{\frac{g}{a} - \frac{1}{2}k} \left(1 \mp \omega\sqrt{\frac{a}{g}}\right), \quad (7)$$

if the square of k be neglected. If ξ , η be Cartesian co-ordinates referred to fixed axes through O , the complete solution is

$$\xi + i\eta = \zeta e^{i\omega t} = C_1 e^{\rho_1 t + i\sigma t} + C_2 e^{\rho_2 t - i\sigma t}, \quad (8)$$

$$\text{where } \sigma = \sqrt{\frac{g}{a}}, \quad \left. \begin{matrix} \rho_1 \\ \rho_2 \end{matrix} \right\} = -\frac{1}{2}k \left(1 \mp \omega\sqrt{\frac{a}{g}}\right). \quad (9)$$

If this be put in real form we perceive that the motion is made up of two superposed circular vibrations, in opposite directions, of period $2\pi/\sigma$; moreover that, if $\omega^2 > g/a$, ρ_1 is positive, so that that circular vibration whose sense agrees with ω continually increases in amplitude. The particle works its way outwards in an ever widening spiral path, approximating to the stable position of relative equilibrium indicated by (3).

3. The next illustration is of a more practical character, and admits of being realised with considerable exactness. A pendulum symmetrical about a longitudinal axis hangs by a Hooke's joint from a vertical spindle which is made to rotate with a constant angular velocity ω . The pendulum used by the writer was constructed originally without any reference to the

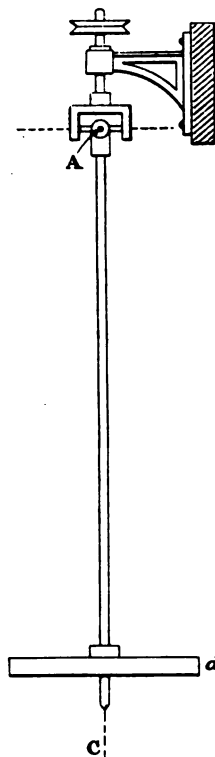


FIG. 1.

present question; no special pains were taken with the Hooke's joint, and the friction there was appreciable. Under these conditions, the instability of the

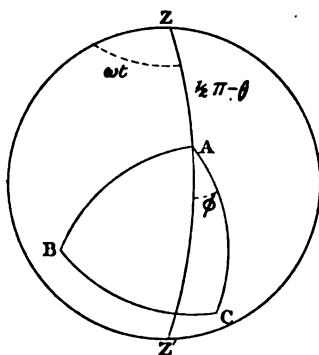


FIG. 2.

vertical position when the rotation ω exceeds a certain critical value becomes rapidly apparent; the originally vertical axis of the pendulum describes an ever widening cone, tending towards the inclined position in which it can rotate as one body with the spindle. To examine the problem mathematically, let θ denote the inclination of one arm A of the joint, the other arm being, of course, horizontal, and let ϕ be the angle which a plane through the axis A and the axis of symmetry (C) makes with the vertical plane through A. The kinetic energy is then given by

$$2T = A(\dot{\phi} + \omega \sin \theta)^2 + B(\dot{\theta} \cos \phi - \omega \cos \theta \sin \phi)^2 + C(\dot{\theta} \sin \phi + \omega \cos \theta \cos \phi)^2, \quad (10)$$

where A B C denote the principal moments of inertia of the pendulum at the centre of the joint. Hence, if $A = B$, we have

$$V - T_0 = -Mgh \cos \theta \cos \phi - \frac{1}{2} \omega^2 \{A - (A - C) \cos^2 \theta \cos^2 \phi\}, \quad (11)$$

provided h denote the distance of the centre of gravity from the joint. This expression ceases to be a minimum for $\theta = 0$, $\phi = 0$, if

$$\omega^2 > \frac{Mgh}{A - C}, \quad (12)$$

and the only stable positions are then those in which the pendulum makes an angle χ with the vertical, given by

$$\cos \chi = \cos \theta \cos \phi = \frac{Mgh}{(A - C) \omega^2}. \quad (13)$$

To examine the motion about the vertical position we neglect, in (10), terms in θ and ϕ of higher order than the second. Thus

$$2T = A(\theta^2 + \phi^2) + 2A\omega(\theta\dot{\phi} - \dot{\theta}\phi) + 2C\omega\dot{\theta}\phi + (A - C)\omega^2(\theta^2 + \phi^2) + \text{const.}, \quad (14)$$

$$2V = Mgh(\theta^2 + \phi^2). \quad (15)$$

Hence Lagrange's equations give

$$\left. \begin{aligned} A\ddot{\theta} - (2A - C)\omega\dot{\phi} - \{(A - C)\omega^2 - Mgh\}\theta &= 0, \\ A\ddot{\phi} + (2A - C)\omega\dot{\theta} - \{(A - C)\omega^2 - Mgh\}\phi &= 0. \end{aligned} \right\} \quad (16)$$

As in the case of (4), we find that these are satisfied by

$$\theta + i\phi = Fe^{i\sigma t}, \quad (17)$$

provided $A\sigma^2 + (2A - C)\omega\sigma + (A - C)\omega^2 - Mgh = 0,$ (18)

or $\sigma = -\left(1 - \frac{C}{2A}\right)\omega \pm \frac{\sqrt{(C^2\omega^2 + 4AMgh)}}{2A}.$ (19)

The vertical position is therefore "ordinarily" stable, whatever the value of ω .

It is evident that θ, ϕ are the rectangular co-ordinates, relative to rotating axes, of a point on the axis of the pendulum. For the corresponding co-ordinates relative to fixed axes we have

$$\xi + i\eta = (\theta + i\phi)e^{i\omega t} = Fe^{i(\sigma + \omega)t}, \quad (20)$$

where $\sigma + \omega = \frac{C\omega \pm \sqrt{(C^2\omega^2 + 4AMgh)}}{2A}.$ (21)

The motion is therefore made up of two superposed circular vibrations of different periods $2\pi/(\sigma + \omega)$, the more rapid vibration being the one whose direction of revolution agrees with that of the spindle.

To investigate the question of permanent stability we introduce into the left-hand members of (16) terms $k\theta, k\phi$ to represent the viscous forces at the joint. The modified equations are satisfied by

$$\theta + i\phi = Fe^{\lambda t}, \quad (22)$$

provided $A\lambda^2 + \{(2A - C)i\omega + k\}\lambda - \{(A - C)\omega^2 - Mgh\} = 0.$ (23)

If σ_1, σ_2 be the two values of σ given by (19), this may be written

$$A(\lambda - i\sigma_1)(\lambda - i\sigma_2) + k\lambda = 0, \quad (24)$$

The two roots of which are, if we neglect the square of k ,

$$\lambda_1 = i\sigma_1 - \frac{k\sigma_1}{A(\sigma_1 - \sigma_2)}, \quad \lambda_2 = i\sigma_2 - \frac{k\sigma_2}{A(\sigma_2 - \sigma_1)}. \quad (25)$$

When $\omega^2 < Mgh/(A - C)$ the two values of σ have opposite signs, and the real parts of λ_1, λ_2 are both negative. The vertical position is then permanently, as well as "ordinarily" stable. But if $\omega^2 > Mgh/(A - C)$ both values of σ are negative, and if σ_1 be the smaller in absolute magnitude, the real part of λ_1 will be positive, and that of λ_2 negative. If we pass to fixed axes, writing as before

$$\xi + i\eta = (\theta + i\phi)e^{i\omega t} = Fe^{(\lambda + i\omega)t}, \quad (26)$$

We find that the periods of the two circular vibrations are to a first approximation unaffected by a small degree of friction, but that the amplitude of one of these vibrations, viz., the one whose direction of revolution agrees with that of the spindle, increases exponentially with the time, whilst the amplitude of the other sinks asymptotically to zero. These points

are illustrated in a striking manner by the apparatus referred to.* Substantially the same experiment can be made in a simpler form by means of a heavy metal ball hanging by a stout string from a hook at the lower end of the spindle. If due precautions be taken to check the violent evolutions which the ball is sometimes apt in the first instance to perform, the torsion of the string soon brings the latter into a state of steady rotation about a vertical diameter, with practically the angular velocity of the spindle. When the steady state has been attained the ball may be left to itself, with the string vertical. The friction of motion relative to the spindle is in this form of the experiment very slight, and although a close observation may soon detect the tendency to a circular vibration of continually increasing amplitude in the direction of revolution of the spindle, some time may elapse before this becomes really conspicuous. The final result is, however, unmistakable.†

4. The question is not seriously modified by a slight amount of deviation from the theoretical conditions, *e.g.*, in the problem of § 3, by a slight defect of alignment between the axis of rotation of the spindle and the centre of the joint. The configuration of relative equilibrium about which the observed oscillations take place is only slightly altered, except in the case of approximate agreement between the imposed period of rotation and what would be the natural period of vibration in the absence of rotation.

The effects of a want of perfect alignment in § 3 can be studied in their simplest form if we neglect the moment of inertia (*C*) about the axis of the pendulum. The case is then that of a particle suspended from the lower surface of a horizontal disc, which is made to rotate about a vertical axis. If l be the length of the string, and a the distance of the point of suspension from the axis of rotation, the inclination α of the string to the vertical in a position of relative equilibrium is given by

$$\frac{g}{\omega^2 l} = \cos \alpha + \sin^3 \beta \cot \alpha, \quad (27)$$

$$\text{where } \sin^3 \beta = a/l. \quad \text{If } \frac{g}{\omega^2 l} < \cos^3 \beta, \quad (28)$$

this has *three* solutions, for two of which $\sin \alpha$ is negative; in one of these, moreover, $\sin \alpha$ is numerically greater, and in the other numerically less,

* It may be worth while to give roughly the dimensions. The steel rod shown in fig. 1 had a length of 36 in. and a thickness of $\frac{1}{2}$ in. The diameter of the iron disc d which could be fixed in various positions along the rod was 7 in. and its thickness $\frac{1}{2}$ in. The spindle was driven from a small electromotor, by means of the small pulley shown, at speeds ranging up to about 25 revolutions per second.

† In a typical experiment the ball was 3 in. in diameter, and was suspended by a string 33 in. long; and the speed was about 7 revolutions per second. The circular vibration took about 18 minutes to attain an amplitude of 1 inch.

than $\sin \beta$. These three positions are shown in fig. 3. The position is found to be both "ordinarily" and "permanently" stable, whilst the position III is on either reckoning unstable. Case II is "permanently" unstable, but the question of "ordinary" stability is less simple. For sufficiently great values of ω the equilibrium may become unstable from this point of view, but there is no difficulty in adjusting the conditions so that

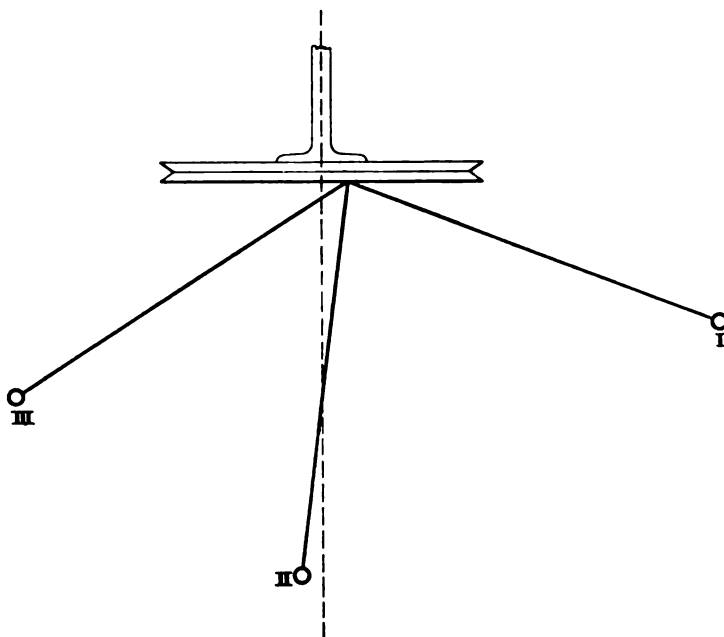


FIG. 3.

there may be "ordinary" stability with "permanent" instability. This was illustrated by an experiment in which the excentricity (a/l) was purposely made appreciable. The metal ball referred to was suspended by a stout string about 3 feet long from a point 1 inch out from the centre of the rotating disc. If the ball be carefully steadied in the central position before being left to itself, its subsequent demeanour differs in no essential way from what is observed when the suspension is made as nearly axial as possible.

5. The next example is one in which the number of degrees of freedom is infinite. For a reason to be given it is hardly a practical one, but it may serve to illustrate the limitations to which the application of the theory is subject. We consider a cylindrical shaft rotating in fixed bearings placed at isolated points, and the question is at what speed the straight form becomes unstable. If the circumferential velocity of the shaft be

small compared with the elastic wave-velocities of the material, the angular momentum about the axis may be ignored. Under this condition it is obvious that the straight form is "ordinarily" stable, the fact of the rotation being irrelevant. To investigate the "permanent" stability, consider, for definiteness, a length l between two bearings A, B. If the axis of x be taken along the length of the shaft, and if y denote the lateral deviation, we have, by the usual theory of flexure,

$$V = \frac{1}{2} E \kappa^2 S \int_0^l y''^2 dx, \quad (29)$$

$$T_0 = \frac{1}{2} \rho \omega^2 S \int_0^l y^2 dx, \quad (30)$$

where S is the cross-section, κ is the radius of gyration about a diameter, E denotes Young's modulus, and ρ is the density of the material. Hence,

$$\begin{aligned} V - T_0 &\propto \int_0^l (y''^2 - m_0^4 y^2) dx \\ &\propto \left[y' y'' - y y''' \right]_0^l + \int_0^l (y^{iv} - m_0^4 y) y dx, \end{aligned} \quad (31)$$

$$\text{where} \quad m_0^4 = \frac{\rho \omega^2}{E \kappa^2}. \quad (32)$$

The integrated terms vanish if each end be either free, or merely supported, or fixed also in direction. It is known from the ordinary theory of transversal vibrations* that any arbitrary function y which is subject to the given terminal conditions can be expanded, for $0 < x < l$, in a series of normal functions,

$$y = C_1 u_1 + C_2 u_2 + \dots \quad (33)$$

Here u_1, u_2, \dots satisfy the differential equations

$$u_1^{iv} = m_1^4 u_1, \quad u_2^{iv} = m_2^4 u_2, \quad \dots, \quad (34)$$

and the proper terminal conditions, m_1, m_2, \dots , being the roots of a certain transcendental equation,† arranged in ascending order of magnitude. If we substitute from (33) in (31), and omit terms which vanish in consequence of the orthogonal property of different conjugate functions, we find

$$V - T_0 \propto (m_1^4 - m_0^4) C_1^2 \int_0^l u_1^2 dx + (m_2^4 - m_0^4) C_2^2 \int_0^l u_2^2 dx + \dots \quad (35)$$

* See Rayleigh, 'Theory of Sound,' chap. viii.

† Thus, if the shaft be merely supported at the ends, the equation is $\sin ml = 0$; if it be fixed in direction at one end and free at the other, we have $\cos ml \cosh ml + 1 = 0$.

The frequencies ($\sigma/2\pi$) of the various modes of natural vibration of the shaft are determined by the relation

$$\sigma_r^2 = \frac{E\kappa^2}{\rho} \cdot m_r^4. \quad (36)$$

Hence $V - T_0$ is a minimum, in the straight condition, or the equilibrium is permanently stable, only so long as $m_0^4 < m_1^4$, *i.e.*, so long as the period of rotation is greater than that of the gravest mode of transverse vibration. The incipient stages of the instability might be studied as in the previous problems. The motion can be analysed into circular vibrations, and it appears that the amplitude of one at least of these, having the same direction of revolution as the shaft, should increase exponentially with the time, provided m_0 exceed the smallest root of the transcendental equation which determines m .

We conclude that a truly symmetrical shaft, rotating accurately about its axis, in rigidly fixed bearings, with any speed exceeding that of the gravest mode of transverse vibration, would be rendered unstable by viscous forces affecting the *relative* motion, such as are, in fact, present owing to the internal friction of the substance. The instability might, indeed, take time to develop itself, but the result would be inevitable. The fact that shafts can be, and are, safely driven at speeds exceeding the critical limit thus indicated* must be ascribed to the operation of dissipative forces (so far ignored) affecting the absolute as well as the relative vibrations. The seat of such forces is probably to be found in a yielding of the bearings. For a similar reason the "permanent" instability illustrated by the experiments of §§ 2, 3 above might be wholly masked if the resistance of the air were very much greater than it actually is, or if the whole apparatus were immersed in a viscous liquid.

* The observed "whirling" of shafts at a series of critical speeds is due to a want of absolute symmetry, and is to be regarded as a forced oscillation of exaggerated amplitude, due to approximate synchronism. (See Dunkerley, 'Phil. Trans.,' A, vol. 185, 1894; Stodola, 'Die Dampfturbinen,' Berlin, 1904, p. 157.)

Prominence and Coronal Structure.

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Physics Observatory, South Kensington.

(Communicated by Sir Norman Lockyer, K.C.B., LL.D., Sc.D., F.R.S., Director
of the Solar Physics Observatory. Received December 2, 1907,—Read
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[PLATE 3.]

The routine work with the spectroheliograph of the Solar Physics Observatory since the year 1904 has been to secure daily, if possible, not only photographs of the sun's disc in the "K" light of calcium, but also of the prominences round the limb at the same wave-length.

To obtain the limb photographs, much longer times of exposure are necessary, so that, in consequence of unfavourable weather conditions, the number obtained is not so great as that in the case of discs.

Many and varied have been the shapes of the prominences recorded, and occasionally some have indicated a pronounced "arched" or "partially arched" form, as shown in a few examples here brought together in Plate 3, figs. 1 to 6.

All the photographs on this plate, including figs. 7 and 8, are on the same scale, and I am indebted to Mr. J. P. Wilkie, the photographer to this observatory, for enlarging them.

It was not, however, until July 17 of the present year that a photograph was obtained which presented a magnificent series of "arches," "envelopes," or "half rings," as they may be termed. This photograph was secured by Mr. W. Moss, computer in the observatory.

The disturbed area was situated near the south pole of the sun in the eastern quadrant, and two exposures were successfully made, the first at 3 h. 14 m. P.M., G.M.T., and the second at 3 h. 50 m. P.M., G.M.T. These photographs are reproduced in Plate 3, figs. 7 and 8, and both have been enlarged twice from the original negatives. The parallel lighter streaks in each of the reproductions are due to changes in the clearness of the sky as the original photographs were being secured; they have, therefore, no connection with the prominence images recorded.

In the first photograph (Plate 3, fig. 7) the arches are clearly visible and complete, but in the second (Plate 3, fig. 8) they are less visible and partially broken up, in spite of the fact that the second photograph had the better exposure. How long the arches had been in existence previous to the time of securing the first record it is, of course, impossible to say,

but the second photograph clearly shows that a striking alteration had taken place.

A close examination and measurement of the first photograph gives the following results, and the accompanying sketch (fig. 1) is here presented.



FIG. 1.—Diagram to illustrate the more conspicuous features photographed at 3 h. 14 m., July 17, 1907 (see Plate 3, fig. 7).

This sketch has been made by enlarging the original and painting the markings in Chinese white to render them more apparent, as the fainter details may possibly be lost in the reproduction in Plate 3, fig. 7.

The most conspicuous feature of the whole of this disturbed region of the sun is the series of three concentric arches numbered 1, 2, and 3. Their concentric nature seems to suggest that they were produced at one point of initial disturbance, and then moved radially outwards.

The distance between the extremities of number 1 is $1'2$; number 2, $3'6$; and of number 3, $5'8$. Their heights from the chromosphere are about $1'5$, $2'9$, and $3'6$ respectively. It will be noticed that the intensity of the arches along their lengths is not uniform; thus, Arch 3 has five points of increased intensity, while Arch 2 has three such maximum points. The mean width of the matter composing the arches is about $0'3$ to $0'4$.

On the eastern side of these arches there is another distinct semi-oval, numbered 4 in the sketch. This intersects arches numbers 3 and 2, and at the point of crossing 3 a more intense patch is indicated. This arch is much flatter than those previously mentioned, and measures $6'6$ between the extremities on the chromosphere, and has a height of $2'2$. The eastern base of arch number 3 falls nearly midway between the bases of Arch 4.

Turning to the southern side of Arch 3, there will be found two projections of different intensity, marked 7 and 8, which seem with little doubt to be

associated with this system of envelopes; their curvature indicates this very strongly. These projections may have formed the stump or, perhaps, a remnant of another large arch, which possibly was concentric with the envelopes 2 and 3, but which was too faint to show on the photograph, or had already, perhaps, disappeared. Two small filaments are indicated at positions marked 9 and 10.

The enormous extent of this disturbance on the solar limb, taken as a whole, may be gathered from the facts that the extreme photographed portions of it were separated by a distance of $12'7$, while the highest part was $3'6$. Converting these into miles, it is found that its breadth extended over about 353,000 miles, or more than three-quarters of the solar radius, and its height reached about 101,600 miles.

Attention may be drawn here to the fact that there is apparently no large prominence underlying these envelopes which may have given rise to them. Whether there be one just on the near or far side of the limb at this position angle cannot be stated, but no trace of any portion can be seen in the original negative.

Examining now the photograph taken at 3 h. 50 m. P.M. (Plate 3, fig. 8), it will be seen that considerable changes have occurred. Arch number 3 is in evidence by broken portions only, and may not show in the reproduction, and these correspond approximately with those of greater intensity in the sketch (fig. 1). All these portions seem to have risen from the chromosphere, as measurements show that the uppermost part is $4'4$ instead of $3'6$. Arches numbers 2 and 1 are difficult to trace, but remnants of them go to make up the spiral or hook-like form in their positions. The upper portion of this is about $3'7$, which is again further from the chromosphere than it was before ($2'9$). The small prominence numbered 5 is still apparent, but in this photograph it has no longer arch number 4 over it, but only a portion of it. The prominence at 6 is broader, but less definite. The prominences 7 and 8 are still about the same, but somewhat fainter, the filaments 9 and 10 have disappeared, and a small prominence close to the eastern side of 9 has become visible.

So far as I am aware this is the first time that such a series of concentric envelopes has been photographed with the spectroheliograph. This indicates that either this form is a most uncommon feature of prominence material, or that the envelopes very seldom appear broadside-on on the limb, so as to display the arch system to the fullest advantage.

In looking up the literature of the *visual* observations of prominences made by means of the spectroscope, the only reference approaching to an account of prominences taking a ring shape is that given by Sir Norman

Lockyer in his volume on 'Solar Physics.'* There he narrates his observation of the behaviour of the F line, and he was led to conclude that the character of the prominence action he was watching could be expressed in these terms :—

"They were really in this case, as already stated, smoke rings thrown up by enormous circumsolar action."

In a later publication† he suggested, in the following words, that the probable origin of such forms might be violent explosions :—

". . . this falling material is dissociated in its descent before or when it reaches the photosphere; the particles which descend sparsely and gently will be vaporised gently, and those which descend violently and in great masses will be exploded violently."

Prior to 1901 no such envelope system, so far as can be found, had been photographed or even observed during eclipses.

In the eclipse of May 18 of that year, Professor Dyson secured some excellent photographs of the eclipsed sun from his observing station at Pulo Aoer Gavang, on the west coast of Sumatra. In his description of these photographs,‡ he called attention to the following feature :—

"A very remarkable arch in the corona round the large prominence at position angle 145° (measuring N.E. S.W.). Round this prominence three separate arches are shown, one inside the other, their radii being $1'2$, $2'4$, and $3'7$ respectively. They have the appearance of layers of cloud over an eruption."

It is interesting to note that the radii here stated correspond very closely to the values of the heights of the arches measured on the spectroheliograph photograph, namely, $1'5$, $2'9$, and $3'6$, showing that the two phenomena are of about the same order of magnitude.

In the eclipse of 1905, arches of a similar nature were recorded, as will be gathered from the following extracts :—

Thus the Astronomer Royal, who observed, at Sfax, Tunisia, stated :—§

"The inner corona in this eclipse seems to be in a state of turmoil (all round the sun's limb), corresponding to the sun-spot and prominence activity of the sun, oval rings and arched structures above the prominences being a special feature The very bright prominence on the east limb, extending over an arc of more than 30° , associated with oval rings and arches in the corona"

* 'Solar Physics,' p. 403, 1874.

† 'The Chemistry of the Sun,' p. 412, 1887.

‡ 'Roy. Soc. Proc,' vol. 69, No. 454, p. 244, 1902.

§ 'Roy. Soc. Proc.,' A, vol. 77, p. 35, 1906.

Describing the photographs he obtained at Vinaroz, Spain, during the same eclipse, Father Cortie, S.J., wrote* :—

“The lower corona in the neighbourhood of these groups of prominences is very much disturbed. A series of interlacing rings or arches surmounts the group, their mean height being very nearly 3'. The general appearance is that of rings seen more or less edgewise, intersected by dark spaces. There are four such distinct bright edges, almost bright rays, from P.A. +75° to P.A. +85° over the three first prominences of the group.”

At Souk-Ahras, in Algeria, the expedition from the Hamburg Observatory, under the direction of Professor R. Schorr, also secured a series of large-scale photographs of the corona at this eclipse. Professor Schorr also photographed† these cloud-like envelopes, as will be gathered from the following extract :—

“The form of the inner corona over the prominence region on the east limb shows a specially interesting appearance. Three to four oval ring-shaped cloud-like envelopes are conspicuous, which are situated at a distance from 4' to 6' over the prominence and can be concluded to be distinctly connected with the eruption of the prominence. This is the first instance to my knowledge in which such an influence of a prominence on the form of the corona has been indicated.”

The above extracts demonstrate clearly the arch-like forms photographed and indicate the close association of these forms with the structure of the lower corona and with the proximity of prominences.

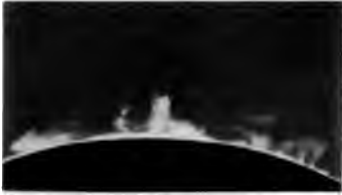
One of the most prominent features of the lower portions of some coronal streamers is that they are made up of groups of in-curving structure, or, as Ranyard termed them, “synclinal” groups. It seems very probable, therefore, that we have in these “envelope” forms the origin of this particular structure.

Although the “envelopes” have been associated with both the corona and prominences in the extracts given above, no statement has been made as to whether they were composed of coronal or prominence material. Such a differentiation is not easy to make by means of photographs taken with a coronagraph, because the images which fall on the sensitive plate are made up of integrated light. The case is different with regard to photographs taken with objective prism cameras, because in these instruments a series of monochromatic images is recorded.

With the object of trying to find out whether these envelopes had been secured by the prismatic cameras in the eclipse of 1905, I have closely examined the negatives which I obtained with a six-inch three-prism

* ‘Roy. Irish Acad. Trans.,’ vol. 33, section A, part 1, p. 20.

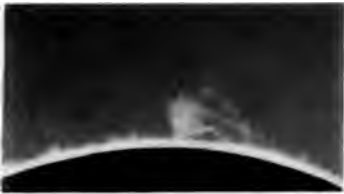
† ‘Mitteilungen der Hamburger Sternwarte,’ No. 10, Hamburg, 1905, p. 29.



1



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3



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prismatic camera at Palma, Majorca, where the Solar Physics Observatory's Eclipse Expedition was stationed.

In the region about the large group of prominences in the north-east quadrant no trace of any images resembling envelopes could be found in either the "H" or "K" radiations of calcium. A similar examination of the green coronal ring at $\lambda 5303.7$, which in one of the photographs is quite strong all round the moon, fails also to show any indication of these envelopes. Their absence may possibly be due either to the small intensity of the envelopes themselves or to the shortness of the time available for exposure.

The fact that "envelopes" similar in form to those described above have now been photographed in the "K" light of calcium by means of the spectroheliograph indicates that the material composing those recorded at the two eclipses contained calcium, like the prominences, as at any rate one constituent. Fortunately, the spectrum of the corona has no line at the wave-length of "K," so the evidence that the envelopes are composed of prominence matter is very strong.

It may be stated, in conclusion, that we have now another link in the chain of evidence to show the dependency of the form of the corona on prominence activity, and this strengthens the view I put forward in 1903,* which was that the different forms of the corona seen and photographed during eclipses depended on prominence and not on sun-spot action.

Addendum, December 11, 1907.

Since the above paper was communicated to the Society, I find that an 'arch' over a prominence was photographed during the eclipse of 1898. It was situated over the flame-like prominence in the south-east quadrant and was photographed at Sahdol, India, with the Thompson coronagraph by the Astronomer Royal, who has kindly notified me of the fact.

DESCRIPTION OF PLATE.

PLATE 3 illustrates some prominences photographed at the Solar Physics Observatory.

FIGS. 1—6 represent some "arched" or "partially arched" forms.

FIGS. 7 and 8 show the system of "envelopes" recently recorded.

The following are the dates and times when each of the prominences were photographed :—

| | | |
|-------------|-----------------|------------------|
| Fig. 1..... | 1905, Sept. 8, | 12 h. 11 m. P.M. |
| „ 2..... | 1907, July 15, | 10 30 A.M. |
| „ 3..... | 1904, July 14, | 12 9 P.M. |
| „ 4..... | 1904, July 19, | 3 52 „ |
| „ 5..... | 1907, July 17, | 3 14 „ |
| „ 6..... | 1904, Sept. 21, | 12 23 „ |
| „ 7..... | 1907, July 17, | 3 14 „ |
| „ 8..... | 1907, July 17, | 3 50 „ |

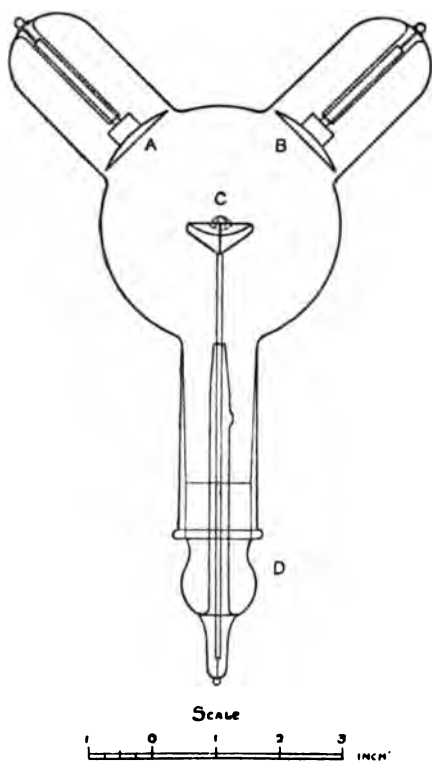
* 'Monthly Notices R.A.S.,' vol. 63, No. 8, p. 481.

*The Conversion of Diamond into Coke in High Vacuum by
Cathode Rays.*

By the Hon. CHARLES A. PARSONS, C.B., F.R.S., and ALAN A. CAMPBELL
SWINTON.

(Received December 10, 1907,—Read January 16, 1908.)

The objects of the experiment were three-fold: firstly, to ascertain whether a diamond could be entirely converted into coke or graphite by heating in a vacuum by cathode rays; secondly, in the event of this being found practicable, to make a determination by Féry's optical pyrometer of the temperature at which the conversion takes place; thirdly, to endeavour to ascertain if, during the conversion, any gas was emitted or absorbed by the carbon.



The vacuum tube employed is shown in the illustration, where A and B are the two aluminium electrodes, C the diamond and D an air-tight ground-glass stopper joint, through which the diamonds were introduced. Alternating current was employed, each of A and B acting as cathode and anode in turn, while their concave curvature was such as to accurately focus the cathode rays on to the diamond. The latter was supported on a plate of iridium, which, in turn, rested in a platinum cup, this arrangement being designed to prevent any stray cathode rays which might miss the diamond from striking the glass walls of the tube and melting the latter. During the experiment the tube was connected to two mercury

pumps of the Toepler type, and in connection with the tube there were also attached two spectrum analysis discharge tubes for the purpose of collecting and examining some of the residual gas in the tube, both before and after the conversion of the diamond into coke.

The alternating current from the mains, which was of 85 periods per second, was passed through the primary of a 10-inch Rhumkorff coil, with the contact-breaker and condenser disconnected, with an adjustable choking

coil in series in the primary circuit, so that the secondary voltage could be varied from about 5000 to 12,000 volts. A reflecting milliamperemeter was employed to read the current through the tube, while the volts across the tube's terminals were measured by an electrostatic voltmeter.

Two diamonds, each about 0.2 inch in diameter, were experimented with. The first was entirely converted into coke without difficulty, while in the case of the second the process was stopped when most of it had been so converted, the residue being black throughout its mass. As the proper degree of vacuum was reached by working the mercury pumps, and as the volts were raised, the diamond in each case became red, and then intensely white hot, till, with about 8000 volts and 44 milliamperes (352 watts) passing through the tube, the diamond began to throw off small sparks. On the volts being increased to 9600, and the current rising to 45.5 milliamperes (436 watts), the sparks thrown off became more numerous and the diamond commenced to become black. Finally, with 11,200 volts and 48 milliamperes (537 watts), a rapid disintegration of the diamond took place, with considerable increase in volume, the residue having much the appearance and consistency of coke.

The temperature of the diamond, as given by the pyrometer during disintegration, was 1890° C.

During the heating up of the diamond and of the tube, large amounts of gas were driven off, and had to be pumped out, but there was nothing to indicate that any of this gas originated from the diamond rather than from the metal parts and glass walls of the tube. Two experiments were made, and in the latter there was distinct indication of a rise in vacuum just about the time of the conversion. These rises in vacuum are, however, not unusual in tubes in which there is highly heated metal, and it was impossible to decide whether any of the absorption of gas took place in the diamond.

In the experiment in question, one of the spectrum discharge tubes was sealed off just before the conversion, when the diamond was commencing to blacken on the surface, while the other was sealed off after the diamond had been converted into coke. These two tubes, therefore, respectively contained samples of the residual gas before and after the conversion. Their spectra have been photographed alongside of one another, but though they are not altogether the same, the differences do not appear sufficiently marked to determine with exactitude any variation in the nature of the gases present.

The experiments were arranged and carried out by Mr. Swinton at his laboratory in London.

On the Scattering of the β -rays from Uranium by Matter.

BY J. A. CROWTHER, B.A., St. John's College, Cambridge.

(Communicated by Professor J. J. Thomson, F.R.S. Received and Read
December 12, 1907.)

Introduction.

The absorption of the β -rays from radio-active substances during their passage through matter has, at various times, attracted a considerable amount of attention from various physicists. Strutt,* for example, made some observations on the absorption of the β -rays from radium by thin sheets of various substances, and, later, Rutherford† performed similar experiments, using the β -rays from uranium. Subsequently the present author‡ made an exhaustive survey of the subject by measuring the absorption of the β -rays from uranium for nearly all the procurable elements, and numerous compounds.

The results obtained may be briefly summarised as follows :—

- (i) The absorption for a given substance may be represented by the equation

$$I/I_0 = e^{-\lambda d},$$

where I_0 is the initial intensity of the β -radiation, I the intensity after traversing a plate of material of thickness d , and λ the coefficient of absorption for the substance.

- (ii) If ρ is the density of the absorbing substance, then for the chemical elements λ/ρ is a periodic function of the atomic weight, the periods corresponding strictly to those of the chemical periodic classification.
- (iii) The value of the ratio λ/ρ is an additive atomic property, depending only on the nature of the atom, and not upon its state of chemical combination.

The methods employed in all the above experiments were substantially the same. A uniform layer of the radio-active substance was prepared, and covered with a sufficient thickness of aluminium foil to cut off completely all the α -radiation. Sheets of the different substances of different thicknesses were then placed directly over the plate of radio-active material, and the

* Strutt, 'Nature,' vol. 61, p. 539, 1900.

† Rutherford, 'Radio-activity,' p. 114, 1904.

‡ Crowther, 'Phil. Mag.,' October, 1906, p. 379.

amount by which the ionisation in an ionisation chamber placed directly above was reduced was measured in some suitable way.

The incident rays thus enter the absorbing plate over an entire solid angle of 180° , while the emergent rays are measured over an angle which depended upon the shape and position of the ionisation chamber, but which was always large. In the experiments of Rutherford all the emergent rays, over the whole solid angle of 180° , entered the ionisation chamber. In those of the present author the angle included amounted to about 90° . The results obtained in the two cases were practically identical.

This method may be correctly said to measure the absorption of the β -rays by the absorbing plate, as it does in fact measure the energy lost by the stream of β -corpuscles in passing through it, under the conditions of the experiment, assuming that the ionisation produced is a measure of the energy of the rays. If the rays alter appreciably in velocity in passing through matter, this latter assumption is not correct, as the ionising power of the rays depends upon their velocity as well as upon their energy.

Schmidt,* however, who has very recently made some direct experiments upon this point, was unable to detect any alteration in the velocity of the β -rays after passing through a thin sheet of aluminium, and his experiments are supported by those of Lenard, who obtained a similar result for cathode rays.

In addition to the absorption as measured by these methods, there is another quantity of importance in the theory of the passage of β -rays through matter, namely, the scattering of the primary beam during its passage through the substance. The β -corpuscles of the incident beam, owing to their high velocity, are able to penetrate the atom, and will thus come into collision with the negative electrons contained in it. At each collision the moving corpuscle will be more or less deflected from its original path, the amount depending upon its velocity and its distance from the deflecting electron. In this way, an incident beam, originally parallel, will become scattered or diffused, during its passage through matter. Some of the incident β -corpuscles may, in fact, after one or more collisions, be deflected through more than a right angle, and, emerging again on the side of the plate at which they entered, make their appearance as return radiation. The scattering may be defined and measured as follows:—

Let ABCD (fig. 1) be a narrow parallel pencil of β -rays, and let I_0 be the intensity of β -radiation crossing the section CD of the pencil parallel to the beam. Suppose, now, a thin sheet of the absorbing substance is inserted in the path of the beam, at XY. Owing to the collisions of the

* 'Physik. Zeit.,' June 1, 1907.

β -corpuscles in the rays with the corpuscles in the absorbing medium, the rays will be more or less scattered and bent away from their original direction. Let I represent the intensity of the radiation parallel to the

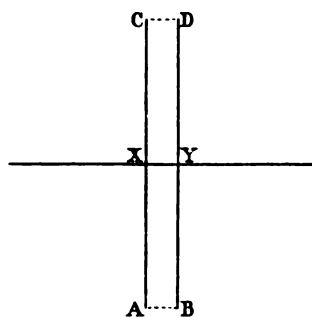


FIG. 1.

original beam passing through the same area CD, after the insertion of the absorbing plate at XY. Then I/I_0 will afford a measure of the amount of scattering undergone by the incident beam during its passage through the absorbing plate.

An optical analogy may make the idea somewhat clearer. Suppose ABCD is a parallel beam of light, and a plate of ground glass is inserted at XY in the place of the absorbing medium. The ground glass will diffuse or

scatter the rays, and the ratio of the intensity of the light passing through the small cross section CD of the original beam, to the original intensity of the beam at CD, will give a measure of the amount of scattering produced by the glass. If, however, instead of measuring the amount of light passing through the small area CD, we measured the total amount of light passing out through the upper face of the ground-glass plate, we should get a measure of the amount of light energy absorbed in the glass, and the two results would be in general very different.

The former corresponds to what we have called the "scattering" of the β -rays, the latter to the "absorption."

McClelland,* using the β -rays from radium, has very recently measured the absorption of these rays, by letting a nearly parallel beam fall upon a metal plate at normal incidence and measuring the whole amount of radiation which emerges on the further side of the plate. The results obtained are very nearly the same as those obtained by the earlier methods. As the whole of emergent rays were measured, this method also measures the absorption and not the scattering of the rays.

Experimental.

It was decided, therefore, to undertake a series of measurements on the scattering of the β -rays by the method outlined above. It is, of course, impossible to obtain an absolutely parallel beam of β -rays. If, however, the radio-active material forms a layer at AB (fig. 1) we can, by limiting the rays by a metal tube ABXY, sufficiently thick-walled to be impenetrable to β -rays, obtain an approximation to our theoretical beam, which becomes

* McClelland, 'Roy. Dublin Soc. Trans,' vol. 9, part IV, 1907.

more nearly exact as we increase the ratio of the length (AX) to the diameter (XY). In the actual experiments the diameter XY was rather less than 0.5 cm.; the length AX was 3 cm., and the greatest possible divergence from the normal was thus about 9° . The rays emerging from the absorbing plate XY were limited by an exactly similar tube, so that the rays emerged from the plate into the ionisation chamber over exactly the same angle as that at which the primary beam fell upon the plate.

Uranium was chosen as the source of β -radiation. The intense activity of radium would have rendered it extremely useful for the purposes of the present experiments, and would have enabled the measurements to have been made with the greatest ease. Unfortunately, the β -rays from radium are extremely complex, consisting of rays ranging in velocity from nearly the velocity of light to less than one-tenth of that amount. As the absorption varies very rapidly with the velocity of the rays, it becomes a matter of great difficulty, and much uncertainty, to interpret the results obtained with such a heterogeneous beam.

Uranium, on the other hand, gives a homogeneous beam of β -rays, moving with a velocity, according to the measurements of Becquerel, of about 1.6×10^{10} cm. per second, or about 55 per cent. of the velocity of light. Thus the results obtained by the use of uranium rays correspond to β -corpuscles moving with a definite speed, and are therefore theoretically much more simple than the measurements obtained from the radium rays.

Unfortunately, the amount of radiation given off by uranium is by no means large, and the experimental difficulties involved in its use were therefore considerable. The theoretical advantages of having a homogeneous beam of rays are so great, however, that it was decided to employ uranium, and to overcome the smallness of the effects to be measured by increased experimental care.

The amount of radiation entering the ionisation chamber could be increased in two ways:—

- (1) By using a large number of tubes fastened side by side, to limit the beam, instead of a single tube, as in the theory.
- (2) By using uranium X, the active β -ray constituent of uranium, as the source of radiation. In ordinary uranium salts, in radio-active equilibrium, a very large proportion of the β -rays emitted by the uranium X are absorbed by the rest of the uranium, which, as it emits only α -radiation, may be regarded for our purposes as inactive. By removing this inactive material, we can greatly reduce the amount of absorption taking place in the radio-active layer, and thus largely increase the amount of radiation which leaves it.

Both these methods were employed. The grid (A, A', fig. 2) was constructed as follows. A large number of brass tubes, each 0.5 cm. in diameter and 6 cm. long, were soldered together side by side, to form a bundle of parallel tubes, about 6 cm. in diameter. This bundle was then sawn in half,

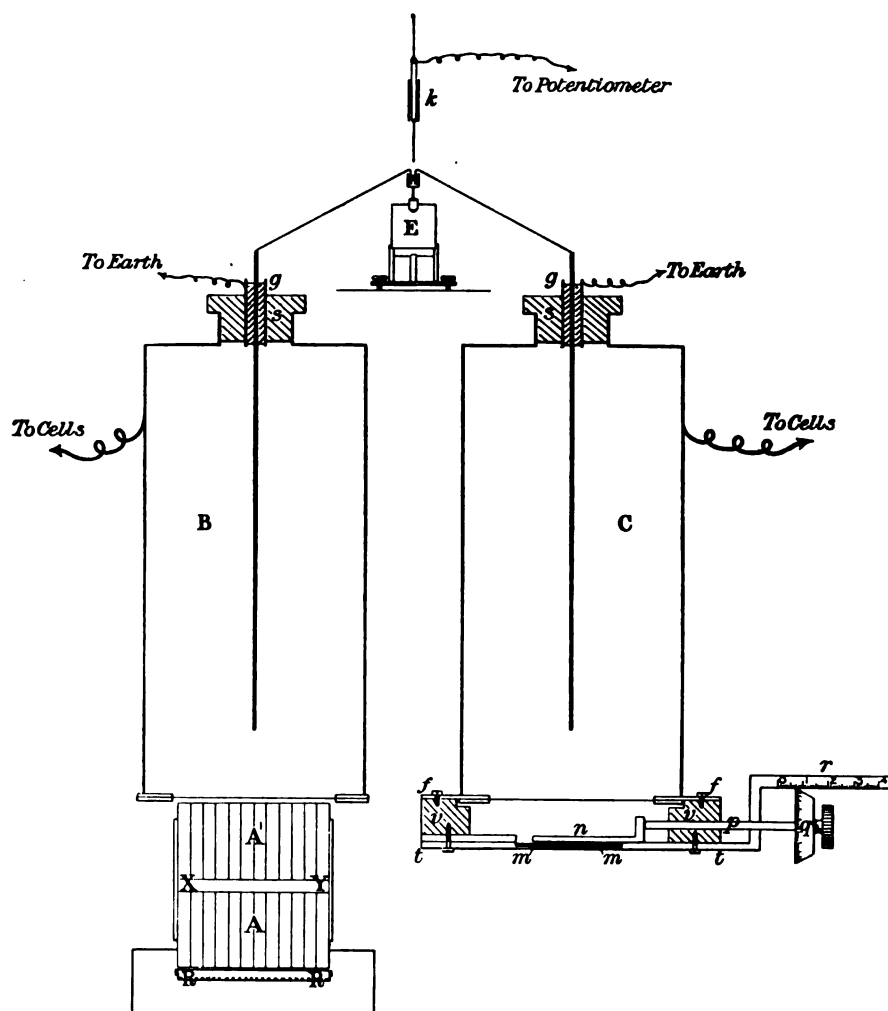


FIG. 2.

at right angles to its length, thus giving two exactly similar grids. These were then mounted, the one over the other, as shown in fig. 2, in exact register, so that each tube in the upper grid was an exact prolongation of one in the lower, a space of 0.5 cm. being left between the two grids for the insertion of the sheets of absorbing material. With this arrangement the

um angle at which the rays could fall upon the absorbing substance, which the rays could leave the substance and enter the ionisation chamber above, was about 9° with the normal. As a measure of the facilities of making measurements by this method it may be mentioned that the insertion of these grids between the layer of radio-active substance in the ionisation chamber cut down the amount of radiation entering the chamber to less than 5 per cent. of its original value.

Various methods were tried for the preparation of uranium X from the uranium compound, including Levin's method of boiling a solution of uranium nitrate with animal charcoal, and incinerating the latter after drying and washing, and Schlundt and Moore's method* of precipitating uranium from various organic solvents by means of ferric hydrate. The method which gave the most satisfactory results in my hands was an extension of the original process by which Sir W. Crookes first isolated the substance.

A considerable quantity (about $\frac{1}{2}$ lb.) of uranium nitrate crystals was dissolved in ether, in a stoppered separating funnel, and the solution well shaken. On allowing to stand, the liquid separates into two layers, a lower aqueous layer and an upper ethereal layer. The former contains a very small proportion of the uranium X, and is carefully run off into a glass dish. About 20 c.c. or so of water are added to the remaining ethereal solution and well shaken up with it to ensure complete mixing. The mixture is then allowed to stand, and the aqueous solution settles to the bottom and is drawn off as before. This process was repeated a third time. In order to check the progress of the separation, each successive washing was vaporated down and its β -ray activity tested. It was found that after three extractions with water the uranium nitrate remaining behind in the ethereal solution was practically inactive as far as β -radiation was concerned.

The three aqueous extracts were mixed together and evaporated down to a few drops of nitric acid until crystallisation occurred. These crystals were redissolved in a small quantity of ether, the solution obtained was placed in a small separating funnel, and treated in exactly the same way as the ethereal solution. The aqueous extracts were again evaporated down and the nitrate converted into red oxide by heating over a bunsen flame. In this way from a large quantity of uranium nitrate there was finally obtained 3 grammes of substance containing nearly the whole of the β -ray activity of the original uranium nitrate.

The powdered oxide was spread in a uniform layer over the bottom of a shallow aluminium tray (R, fig. 2) the exact diameter of the lower grid,

* 'Phil. Mag.,' October, 1906, p. 377.

and covered with a lid of aluminium foil 0.07 mm. thick, in order to exclude any α -radiation. By repeating the process the uranium X might have been obtained in a still purer form. As, however, the amount of oxide after the second purification was only just sufficient to form a thin uniform layer over the bottom of the aluminium tray, it was not considered desirable to carry the process any further. Even when increased in this way the amount of radiation coming through the two grids was so small that special devices had to be employed to measure it with any degree of accuracy.

The chief difficulty in the measurement of small amounts of β -radiation lies not so much, perhaps, in the smallness of the ionisation produced, as in the fact that this ionisation is comparable in amount with the spontaneous ionisation in the ionisation chamber employed. A Wilson inclined electroscope, when carefully adjusted, is an extraordinarily delicate instrument for the detection and measurement of very small currents, and can be made sufficiently sensitive to measure the spontaneous ionisation in a closed vessel of, say, 1 litre capacity to within a few per cent. with ease. However, on making such measurements, I have always found it exceedingly difficult to get consistent results. Successive readings will often differ by 20 per cent. or even more in smaller vessels, although to all appearances the apparatus is working perfectly. Whether this effect is really due to actual variations in the ionisation within the chamber, or whether it is due to some irregularities in the working of the apparatus for very small currents, it is always present. The discrepancies between the different readings become less and less noticeable as the spontaneous ionisation becomes a less and less important part of the whole. When, however, as in the present experiments, the spontaneous ionisation is a very appreciable fraction of the total ionisation to be measured, they are a source of considerable difficulty and a possible cause of error.

It was decided, therefore, to employ a compensation method of measurement, and the result was most satisfactory. Not only was greater sensitivity attained, but the above trouble was almost completely eliminated. The two chambers were constructed of exactly the same size, shape, and materials, and the spontaneous ionisation in the two was very nearly the same. Moreover, the small difference between the ionisation in the two vessels remained practically constant (except for a small diurnal variation, studied recently by Campbell and Wood,* which was just perceptible), and balances could be obtained with accuracy and regularity.

Campbell† has described a compensation method which depends upon the

* 'Phil. Mag.,' February, 1907.

† 'Camb. Phil. Soc. Proc.,' vol. 13, p. 132.

variation produced in the current through a vessel containing uranium oxide, when the pressure in it is altered. This method is very suitable, when used, as by Campbell, for the measurement of small variations in a fairly large ionisation current. It is, however, only sensitive over a small range. It was thus unsuitable for the present experiment.

The principle finally adopted was as follows. A layer of uranium oxide was formed, about 2 mm. in thickness, and covered with sufficient aluminium foil to cut off the α -rays. This was placed beneath a shutter, sufficiently thick to stop all the β -radiation. The amount of radiation from the uranium layer which entered an ionisation chamber placed above could be regulated by opening or closing the shutter so as to expose a greater or smaller area of the radiating layer. This method was found to be not only easy to work, but also very accurate. It may be worth while, therefore, to describe the apparatus more fully. It is shown in section in fig. 2.

A, A' are the pair of grids which have been already described. The uranium X forms a thin layer over the bottom of the shallow aluminium tray R, R, and is covered with a lid of aluminium foil, to cut off all α -rays. The sheets of absorbing substance are inserted at XY. The rays pass upwards through A' into the ionisation chamber B.

B, C are two cylindrical ionisation chambers of exactly the same size and construction. They are closed at the bottom with thin aluminium foil. The central wire electrodes pass out through earthed guard rings g, g , from which they are insulated by sulphur. The guard rings themselves are insulated from the rest of the chamber, which is kept charged to a sufficiently high potential to produce saturation in the ionisation current, by ebonite stoppers, S, S.

C is the ionisation chamber of the compensator; the shutter arrangement is shown below.

N is the shutter itself, constructed of brass of sufficient thickness to cut off all the β -rays from the layer of uranium oxide placed below. This layer was contained in a shallow depression m, m , 2 mm. deep, in a brass plate t , and covered with sufficient aluminium foil to cut off all α -radiation. The shutter n could be moved backwards and forwards across the layer, by means of the screw p . The screw was accurately cut with a $\frac{1}{2}$ -mm. pitch, and the wheel q was graduated into 100 divisions. The shutter could therefore be set, if necessary, to 1/200th mm. The shutter was screwed on to an insulating ring of ebonite v, v , to which the ionisation chamber C was also rigidly attached by means of a projecting flange f .

The ionisation in C, when the shutter was open to its full extent, was many times the maximum ionisation to be measured in B. The radiation

from the uranium oxide layer m , m was therefore cut down by aluminium screens, until the radiation in C was equal to that in B, when the shutter was open to a suitable extent, say about 3 cm.

The compensator was, of course, carefully calibrated, by measuring the actual rate of leak through the chamber C, with the shutter open to different amounts. The rate of leak was, in fact, found to be very nearly proportional to the area of uranium oxide exposed.

It seemed clear, from the construction of the compensator, that the shape of the calibration curve would depend only upon the arrangement of the shutter, and would be independent of the radiating power of the layer of uranium oxide below. It should thus have the same shape, whether the layer was covered by only thin foil, or whether it was screened by a considerable thickness of aluminium. This was found experimentally to be the case. This fact added greatly to the accuracy attainable with the compensator, as the latter could thus be calibrated, using the full amount of β -radiation from the uranium oxide layer (a process which, on account of the amount of ionisation produced, was both easy and accurate) and the radiation could then be screened down to an amount suitable for the purposes of the experiment. Had it been necessary to calibrate the compensator, under the actual conditions under which it was used, those same difficulties would have arisen in determining the calibration curve which it was the object of the compensation method to avoid.

The two ionisation chambers were kept charged to equal, and opposite, potentials, by means of a cabinet of small storage cells; 400 volts were found amply sufficient to produce saturation.

The electrodes of the two ionisation chambers were connected to the same Wilson electroscope E, by wires dipping into a metal cup containing calcium chloride solution, connected to the gold leaf system. The system could be earthed, charged to any required potential, or left insulated by means of the key k , dipping into the cup, which could be operated from a distance. A solution of calcium chloride has been found, in practice, to be preferable to mercury in electroscope keys, as the mercury very rapidly becomes contaminated, and, when not perfectly clean, is very apt to cause a slight "kick," or displacement of the gold leaf, on breaking contact. Calcium chloride solution appears to be quite free from this objectionable property.

The electroscope, of the ordinary Wilson inclined type, was made as sensitive as possible, by a careful adjustment of the potential of the plate, the position of the point of suspension of the gold leaf, and the tilt of the instrument. These electroscopes are somewhat difficult to adjust to sensi-

tiveness, but when once the proper adjustments have been made, they form very delicate detectors of small ionisation currents. The particular electro-scope used in these experiments gave a deflection of from 5 to 10 divisions for 1/50 volt. The capacity of the electro-scope and the two electrodes was less than 10 cm., and, using the null method, a movement of the leaf of one division in 10 minutes could be easily detected. It follows, therefore, that a difference in the currents through the two chambers of about 5×10^{-17} ampere would produce a noticeable disturbance in the balance. It was in practice possible to obtain a balance between the two chambers to an accuracy of about 1 or 2 per cent., except in the case of the thicker sheets, where the radiation was very much reduced.

The method of making an observation was as follows. The sheet whose scattering power was to be measured was placed at XY between the grids, and the shutter was opened out, until, when the system was insulated, there was no appreciable movement of the gold leaf in 10 minutes. The ionisations in the two chambers are then equal and the reading of the shutter is obtained from the scale r and the graduated wheel q .

The sheet was then removed from XY and a balance again obtained. Finally, a thick sheet of lead, sufficient to stop all the β -rays, was placed at XY and the adjustment again made. The spontaneous ionisation in B was slightly greater than in C, and hence a balance could be obtained by slightly opening the shutter. The relative amounts of ionisation corresponding to each of these three shutter readings could then be read off on the calibration curve. The final reading, giving the small excess of the spontaneous ionisation in B over that in C, was subtracted from each of the first two readings. The results when thus corrected gave the relative amounts of radiation entering the chamber B, with and without the absorbing sheet at XY. The ratio I/I_0 , where I is the intensity of radiation entering B when the absorbing sheet is at XY, and I_0 the intensity of radiation when there is no substance between the grids, is plotted against the thickness of the sheet. The curves thus obtained are given in fig. 3.

Various thicknesses of material were used in every case. It was found that the falling off in the intensity of the radiation was much more rapid in this method than in the case of the measurements of the absorption. In fact, the results showed that the scattering of the incident beam was practically complete after passing through a thickness of about 1/10 mm. of aluminium, and thus very thin foil had to be used for the measurements. The number of substances which could be utilised, therefore, was strictly limited.

The thickness of any particular sheet of the material was determined by

finding the weight of a known area of it. The thickness is then given by the formula,

$$d = w/\alpha\rho,$$

where w is the weight of a sheet of area α , and ρ is the density of the substance. In this way, using an accurate balance, the thickness of even the thinnest leaf could be determined with considerable accuracy.

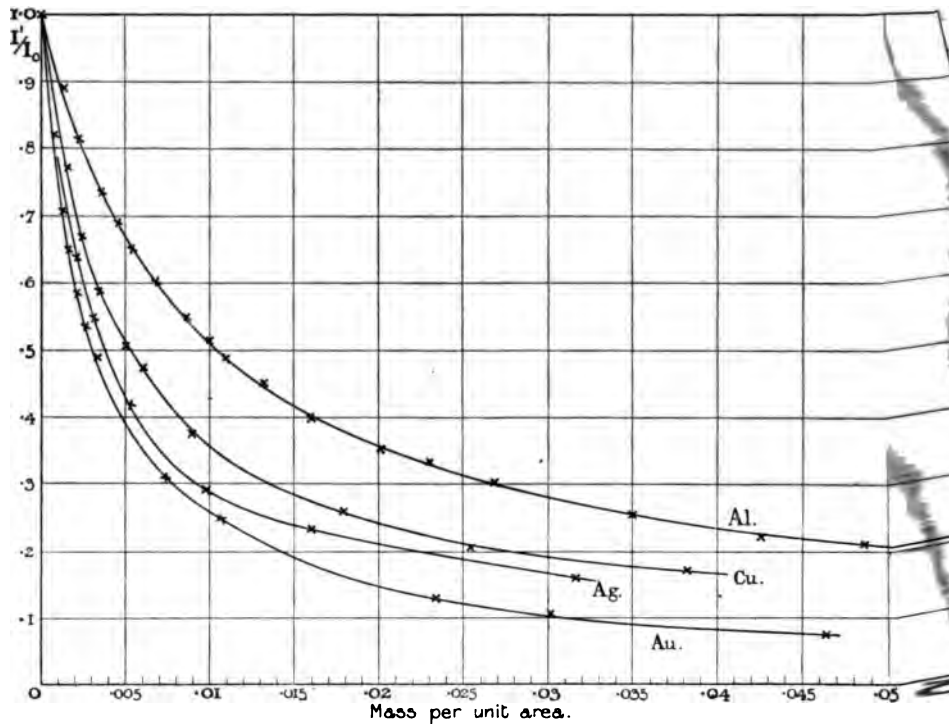


FIG. 3.

It was thought just possible that the shape of the curves obtained might be due to the presence in the uranium rays of some very soft radiation. If the β -rays used contained any considerable quantity of very soft radiation, the absorption curve would very much resemble the curves which were actually obtained. It would, in fact, be the sum of two exponential curves, one of which had a considerably higher index than the other.

If this was the cause, however, we should be able to eliminate the preliminary rapid decrease by placing over the uranium X, but underneath the bottom grid, a thickness of foil sufficient to cut off all the softer rays. We can see from the curve for aluminium that, if the rapid decrease is due to the presence of soft rays, these rays must be all absorbed in a thickness of about 0.15 mm. of aluminium. Accordingly a sheet of aluminium, 0.3 mm. thick, was inserted between the uranium X and the bottom grid

and the experiments repeated. It was found that the insertion of this thickness of aluminium did not make the slightest difference to the results obtained. The curves had exactly the same shape, whether the aluminium plate was present below the grid or not. It is thus clear that the results are not due to any want of homogeneity in the β -radiation employed.

One possible source of error has yet to be mentioned, and is connected with the use of the grids. The β -rays which come from the radio-active layer and fall upon the walls of the tubes of which the grids are composed produce a certain amount of secondary radiation, some of which may fall upon the plate at XY at a greater angle than that of the primary beam. This would tend to diffuse the beam falling upon XY and thus cause a departure from the simple theory. I was unable to discover any method of eliminating this effect, without at the same time reducing the radiation to such an extent as to be quite unmeasurable. The effect is, however, in all probability extremely small. The total return radiation from a plate exposed to uranium β -rays has been shown by the author* to be only a few per cent. of the primary beam for copper, of which the tubes were made. From the nature of the case, only a small fraction of this can fall upon the plate at XY; while a large proportion of the secondary radiation which does fall upon the plate does so at an angle not greater than that of the primary beam. The effect, therefore, cannot be large. It was thought possible also that the air in the tubes composing the grid might have some similar effect in scattering the incident beam.

In order to investigate these effects, a second pair of grids was constructed, as different as possible in these respects from the original grids. In order to reduce the secondary radiation to a minimum, aluminium was used as the material of the grids. Two aluminium plates, each 0.6 cm. thick, were fastened together by screws, and a large number of holes, each 1.5 mm. in diameter, were drilled through the two plates. The plates were then separated by about 3 mm. to allow of the introduction of the metal sheets between them. In this way the total length of the grids was reduced from 6.5 cm. in the case of the first pair to 1.5 cm., while at the same time the secondary radiation from the walls was considerably reduced by substituting aluminium for copper as the material of the grid. The angle of the new grid was somewhat greater than that of the original, amounting to about 14° .

It will thus be seen that the second grids differed in every possible way from the first. The results obtained with the second grid are given in Table IV. It will be seen that they agree very closely with the results obtained with the first grids.

* Crowther, 'Phil. Mag.', October, 1906, p. 391.

The difference between the two sets of values for σ , the coefficient of scattering, does not exceed about 10 per cent. Considering the difficulties of the experiment, and the fact that neither of the grids gives a truly parallel pencil of rays, the agreement is quite satisfactory.

We may fairly assume, therefore, that the results obtained are not due to any peculiarities in the construction or materials of the grid.

Results.

Experiments have been made on various thicknesses of mica, aluminium, copper, silver, and gold. It was found that in order to obtain the desired measurements it was necessary to use very thin foil or leaf. In gold, for example, the scattering of the β -rays was found to be practically complete after passing through a thickness of only 0.0002 cm. The number of substances which could be investigated was therefore very limited. Attempts were made to obtain sufficiently thin sheets of other metals, but without success.

The results obtained are plotted in fig. 3. The ordinates give the values of the ratio I/I_0 , where I is the intensity of the β -radiation entering the ionisation chamber after passing through a thickness d of material, and I_0 the initial intensity of the radiation in the absence of the absorbing plate. In order conveniently to represent all the curves on the same diagram, the abscissæ represent not the thickness d directly, but the corresponding mass per unit area, of the absorbing foil. In order to obtain the thickness d , it is merely necessary to divide these values by the density of the particular substance to which they refer. The curve for mica is not given, as it is almost indistinguishable from the curve for aluminium.

All the curves are similar in type. We will consider the curve for aluminium as typical of the rest.

On looking at the curve (fig. 3) it will be seen that it consists of two portions. In the first part, the curve descends very steeply, showing that the amount of radiation entering the ionisation chamber falls off at first very rapidly as the thickness of the foil is increased. After a certain thickness is reached, however, this effect rapidly dies away, and the curve finally assumes a much more gentle slope.

It can easily be shown, by plotting the logarithm of the ratio I/I_0 against the corresponding thickness d , that the final portion of the curve is exponential in form and may be represented by the equation

$$I/I_0 = Ce^{-\lambda d},$$

where d is the thickness of material traversed by the β -rays, and C and λ are constants.

On calculating the values of these constants for the curve, it is found that the coefficient λ is approximately the same as the "coefficient of absorption," as measured by the earlier methods. It seems clear, therefore, that this final portion of the curve represents a true absorption of the energy of the rays.

The earlier, and much steeper portions of the curve, are equally clearly due to some other cause, and represent, according to the theory of this experiment, the "scattering" of the rays. It is evident from the shape of the curve that the "scattering" takes place in a much less thickness of foil than the absorption. In order to investigate the way in which it varies with the thickness, it is necessary to correct the experimental values for the loss of intensity due to the absorption of the energy of the rays in passing through the particular thickness of foil used.

The amount of this absorption can easily be calculated from the later exponential portion of the curve, assuming that the absorption obeys this exponential law for the thinner sheets also.

The scattering effect for an incident pencil of rays of given intensity I_0 , and for a given substance, is a function only of the thickness of material passed through by the rays. Thus if I' is the intensity of the transmitted beam which would enter the ionisation chamber in the absence of any loss due to absorption of energy, and considering only the loss due to the scattering, we should have

$$I' = I_0 f(d),$$

where $f(d)$ represents some function, at present undetermined, of the thickness d of material passed through by the rays. The intensity of the transmitted beam I'' in the absence of any loss due to scattering of the rays, and considering only the absorption of energy, is, as was shown above, represented by the equation

$$I'' = I_0 e^{-\lambda d}.$$

The actual experimental curve in the presence of both scattering and absorption is, therefore, given by the equation

$$I/I_0 = e^{-\lambda d} \cdot f(d),$$

where I represents the intensity of the beam transmitted through the apparatus, when both the scattering and the absorption of the rays are considered.

Thus representing the experimental value of I/I_0 taken from the curve by y we have

$$y = e^{-\lambda d} f(d),$$

or

$$f(d) = y/e^{-\lambda d}. \quad (1)$$

But λ is known, from the final exponential portion of the curve, and hence we can easily find the values of $e^{-\lambda d}$ for any given value of d , from a table of exponentials. Dividing the values of y from the curve, by the values of the exponential so obtained, we can find the value of $f(d)$ for different values of d .

Table I.—Aluminium.

| d . | y . | $e^{-\lambda d}$. | $y/e^{-\lambda d}$. | $(y/e^{-\lambda d} - C)$. | $\log_{10}(y/e^{-\lambda d} - C)$. — |
|-------|-------|--------------------|----------------------|----------------------------|---------------------------------------|
| cm. | | | | | |
| 0.000 | 1.00 | 1.00 | 1.00 | 0.70 | 1.84 |
| 0.001 | 0.785 | 0.978 | 0.80 | 0.50 | 1.70 |
| 0.002 | 0.655 | 0.958 | 0.68 | 0.38 | 1.58 |
| 0.003 | 0.561 | 0.940 | 0.60 | 0.30 | 1.47 |
| 0.004 | 0.495 | 0.920 | 0.54 | 0.24 | 1.38 |
| 0.005 | 0.450 | 0.900 | 0.50 | 0.20 | 1.30 |
| 0.006 | 0.410 | 0.881 | 0.46 | 0.16 | 1.20 |
| 0.008 | 0.350 | 0.845 | 0.41 | 0.11 | 1.04 |
| 0.010 | 0.303 | 0.811 | 0.37 | 0.07 | 2.85 |
| 0.012 | 0.270 | 0.785 | 0.34 | 0.04 | |
| 0.015 | 0.230 | 0.730 | 0.31 | 0.01 | |
| 0.020 | 0.200 | 0.657 | 0.30 | 0.00 | |
| 0.022 | 0.191 | 0.630 | 0.30 | 0.00 | |

The results of these operations are given in full in Table I for the case of aluminium; the value of λ for aluminium, as obtained from the last portion of the curve, being 21.

The first column gives the thickness d of the absorbing foil in centimetres; the second column y the corresponding experimental values of I/I_0 . The third column gives the values of $e^{-\lambda d}$ for the thicknesses d given in the first column, λ being the coefficient of absorption calculated from the final portions of the curve. The fourth column gives the values of $y/e^{-\lambda d}$, and thus, on the previous theory, shows the true scattering effect of the foil, corrected for the loss due to the absorption of the rays.

It will be seen that the value of the ratio I'/I_0 , where I' has the same significance as before, diminishes rapidly at first, but finally, after passing through a thickness of about 0.015 cm., becomes constant at about 0.30, and is not further diminished by passing through additional thicknesses of the foil. The scattering, in fact, becomes complete. The magnitude of this constant, which we will call C , has no theoretical importance, its value depending upon the construction of the apparatus. If it were possible to work with an infinitely narrow, and accurately parallel, pencil of β -rays, the value of the ratio I'/I_0 would decrease practically to zero. Owing to the necessities of experiment, the construction of the grid allows the rays to emerge into the ionisation chamber, over a finite angle, and hence a finite,

out constant, proportion of the rays enter the ionisation chamber, even when the scattering is complete. The larger the angle over which the rays can merge into the ionisation chamber, the larger will be the value of C . Thus in the case of the aluminium grids the value of C is nearly twice as great as in the case of the first grid of copper tubes.

In order to obtain an approximate idea of the way in which the scattering would vary, in the absence of the disturbing effects due to the finite angle of the grid, we may subtract the constant final value C (which gives the intensity of the radiation which would enter the ionisation chamber when the rays are completely scattered, in the absence of any absorption of the rays) from each of the values of $y/e^{-\lambda d}$ in the table.

The results so obtained are given in the fifth column of Table I. If the logarithms of these numbers are plotted against the corresponding thicknesses, as given in the first column of the table, the resulting curve is very approximately a straight line. The curves thus obtained for the different substances are given in fig. 4. It will be seen that in every case we get approximately a straight line. It appears, therefore, that the scattering, like the absorption, is approximately an exponential function of the thickness, and that it may be expressed by the equation

$$I'/I_0 = e^{-\sigma d},$$

where I_0 is the initial intensity of the β -radiation passing through a small cross section of a parallel pencil of the rays, I' is the intensity of the radiation passing through the same small cross section, when a sheet of metal of thickness d is interposed in the path of the beam (corrections having been made for the diminution in the radiation due to the absorption of energy); and σ is a constant which we may, by analogy, call the *coefficient of scattering* of the rays for the given metal.

The departures of the curve from the exponential are possibly somewhat greater than the probable errors of the readings. They are, however, not greater than might be accounted for by the inevitable departures of the apparatus from the theoretical form.

Assuming that the scattering follows this exponential law, and taking the absorption into account, it is easy to show that the experimental curves could be represented by the equation

$$y = I/I_0 = (1-C)e^{-(\sigma+\lambda)d} + Ce^{-\lambda d}. \quad (2)$$

or we have from the above,

$$y/e^{-\lambda d} - C = ke^{-\sigma d},$$

which, since $y = 1$ where $d = 0$, leads directly to the above expression. The values of λ and C for aluminium have already been obtained, and σ can

readily be calculated from the last column of Table I. It is about 270. By substituting these values in equation 2, we can calculate the values of I/I_0 for different thicknesses of aluminium. A comparison of the values so

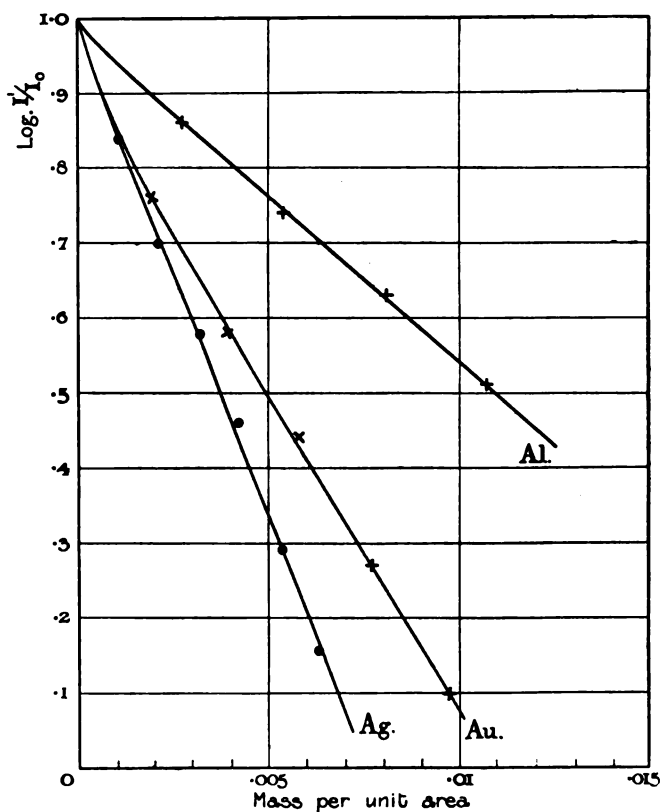


FIG. 4.

calculated, with the actual experimental values, is given in Table II, and affords a test of the accuracy with which the theory fits the experimental results.

It will be seen that the divergence does not amount at most to more than a few per cent. of the initial radiation. Considering the departures of the apparatus from the theoretical form, and the difficulties of the experiment, the agreement is very satisfactory.

So far we have been considering the case of aluminium. The curves for the other substances investigated are, however, exactly the same in form, though with different constants, and may be resolved into the sum of two exponential curves in exactly the same way as the curve for aluminium. It will not be necessary, therefore, to describe them in further detail. The

Table II.—Aluminium.

| Thickness. | I/I_0 | |
|------------|-------------|-----------|
| | Calculated. | Observed. |
| cm. | | |
| 0·000 | 1·00 | 1·00 |
| 0·001 | 0·81 | 0·79 |
| 0·002 | 0·69 | 0·66 |
| 0·003 | 0·58 | 0·56 |
| 0·004 | 0·51 | 0·49 |
| 0·006 | 0·40 | 0·41 |
| 0·008 | 0·36 | 0·35 |
| 0·010 | 0·29 | 0·30 |
| 0·015 | 0·23 | 0·23 |
| 0·020 | 0·20 | 0·20 |

s of σ , λ , and C, for the different substances investigated are given in III. It may be mentioned that the agreement in all cases was at as good as in that of aluminium.

Table III.

| Substance. | σ . | λ . | C. | σ/ρ . | σ/λ . |
|-----------------|------------|-------------|------|-----------------|--------------------|
| Aluminium | 268 | 21 | 0·30 | 99 | 12·8 |
| Carbon | 283 | 21 | 0·30 | 100 | 13·4 |
| Graphite | 2385 | 215 | 0·40 | 267 | 11·1 |
| Silver | 3320 | 250 | 0·34 | 313 | 13·3 |
| Gold | 5100 | 460 | 0·22 | 264 | 11·1 |

Table III gives the values of the coefficients σ and λ as calculated from experimental results; and also the values of σ/ρ , where ρ is the density of the absorbing medium. A further column gives the value of σ/λ . It will be seen at once that σ is much greater than λ , being in general about ten times as great, the ratio being very nearly the same for all substances. The determinations of λ have to be made from the last observations on the curve where the radiation is very much reduced, and the proportional experimental error, therefore, considerably increased, the differences do not amount to much more than the probable error of experiment.

In this case we should expect to get variations in the value of σ/ρ with atomic weight similar to those obtained for the ratio λ/ρ , that is to say, it should be a periodic function of the atomic weight. Sufficient elements have not been measured to test this very thoroughly. It may be pointed out that copper, silver, and gold, which belong to the same chemical group, have nearly the same value for the ratio σ/ρ .

It may be noticed in passing that the values given by this method for the coefficient of absorption λ are somewhat higher than those given by the earlier methods. It was shown in a former paper* that for the heavier elements, such as silver and gold, the absorption in thin sheets was greater than would be expected from the final exponential value calculated from sheets of greater thickness. As the foil used in these experiments was much thinner than that employed in the previous measurements, it seems possible that had it been possible to measure thicker sheets by the present method the values obtained for λ in the two cases might have been more nearly equal.

Table IV.—Aluminium Plate Grids.

| Substance. | σ . | λ . | C. | σ/λ . |
|-----------------|------------|-------------|------|--------------------|
| Aluminium | 236 | 18.5 | 0.51 | 12.8 |
| Gold | 4550 | 390. | 0.44 | 11.7 |

It will be noticed, however, that the values obtained for λ with the aluminium grid are distinctly lower than those obtained when the copper grid was used. It seems probable therefore that at any rate part of the difference is due to the different arrangement of the apparatus in the two series of experiments.

The above results show that a pencil of β -rays is completely scattered in a thickness of matter which is quite small compared with the thickness required to completely absorb them. Thus, taking gold as an example, the rays are practically completely scattered in a thickness of only 0.0002 cm. The absorption in a layer of this thickness only amounts to about 20 per cent. of the initial energy of the rays. It seems evident, therefore, that an appreciable portion of the primary β -rays must emerge again on the same side of the foil and reappear as return radiation. It seems possible that a large proportion, if not the whole, of the return β -radiation (neglecting that set up by the γ -rays) may arise from this effect, and may thus consist principally, if not entirely, of scattered primary radiation. The fact that the return radiation from a metal plate has practically the same velocity as the primary rays seems to lend some support to this conjecture.

While it may thus be possible to explain the return β -radiation from a metal plate, on the hypothesis that it is due to the scattering of the primary rays, it does not appear to be possible to explain the results of the present experiments on the theory that they are due to secondary radiation. McClelland,

* Crowther, 'Phil. Mag.,' October, 1906.

who has worked out the theory of secondary β -radiation very completely in various recent papers in the 'Transactions of the Royal Society of Dublin,' has shown that the effect of secondary radiation would be to produce an increase in the slope of the curve for very thin sheets. On calculating the amount, however, it is at once seen to be much too small to account for the results of the present experiments. Taking the case of lead, which gives the largest effect of any of the metals, and plotting the logarithm of the ratio I/I_0 for different thicknesses, McClelland has shown that the effect of the secondary radiation would be to cause an increase in the slope of this curve in its initial portions to about 1.64 times the final exponential value.* For aluminium the effect of the secondary radiation would be considerably less. In the present experiments, however, the slope of the initial portions of the logarithmic curve is at least 12 times its final value. We must consider, therefore, that the present results are mainly due to the scattering of the primary β -rays, by collisions with the β -corpuscles in the atoms of the absorbing plate, and not to secondary radiation.

In conclusion, we may mention that the results of the present experiments remove what was apparently a serious discrepancy between the absorption of the β -rays of uranium and radio-active materials generally, and the β -rays constituting the cathode stream.

Becker† has measured the absorption for various gases of very fast cathode rays, due to a fall of potential of about 35,000 volts, and having a velocity, therefore, of about 10^{10} cm. per second. The values he obtained for the ratio λ/ρ , where λ is the coefficient of absorption and ρ the density, ranged between 1000 and 3000. The values obtained for the same ratio, using uranium β -rays, which according to Becquerel have a velocity of about 1.6×10^{10} cm. per second, ranged from about 4 to 10. The difference is thus considerably more than can be accounted for by the mere difference in velocity of the rays in the two cases.

The "absorption" of the cathode rays is always measured by finding the falling off in intensity of the rays crossing a small fixed area (namely, the aperture of the Faraday cylinder used in the measurements) when various thicknesses of the absorbing substance are interposed in the path of the beam, the original beam being always a nearly parallel pencil of rays. It will thus be seen that what is actually measured in these experiments corresponds not to the "absorption" of the β -rays, but to the quantity which we have called scattering.

Comparing the results of Becker for the cathode rays with the values

* McClelland, 'Roy. Dublin Soc. Trans.,' vol. 9, part IV, p. 41, 1907.

† 'Ann. der Phys.,' vol. 17, p. 381, 1905.

206 *Scattering of the β -rays from Uranium by Matter.*

obtained in the present paper for σ , the coefficient of scattering of the β -rays, the apparent discrepancy is at once removed. It can be shown on theoretical grounds* that the scattering should vary inversely as the fourth power of the velocity. The β -rays from uranium have a velocity of about 1.6 times that of the cathode rays of Becker. Multiplying the results obtained for σ/ρ in the present experiments, therefore, by $(1.6)^4$, to allow for the difference on velocity of the two kinds of rays, we obtain results varying between 650 and 2100. These numbers agree well with the values, ranging from 1000 to 3000, obtained by Becker for the cathode rays.

Summary.

The results of the present experiments may be briefly summarised as follows:—

- (i) A parallel pencil of β -rays is scattered in its passage through matter, the scattering being practically complete after the rays have traversed a thickness of material which varies from 0.015 cm. for aluminium to 0.0002 cm. for gold.
- (ii) The scattering, after correction for the loss of energy, due to the absorption of the rays, may be represented by an equation of the form $I/I_0 = e^{-\sigma d}$, where d is the thickness of the material traversed by the rays, and σ is the coefficient of scattering for the rays, I_0 being the initial intensity of a narrow parallel pencil of β -radiation, crossing a small fixed cross section of the pencil, and I the intensity crossing the same cross section, when a thickness d of material is placed in the path of the beam at a considerable distance from the fixed cross section.
- (iii) The ratio of the coefficient of scattering σ to the coefficient of absorption λ is approximately constant for all the substances measured, its average value being about 13. The value of the ratio σ/ρ , where ρ is the density, shows similar variations to those for λ/ρ .

In conclusion, I wish to express my best thanks to Professor J. J. Thomson for his kindness in suggesting to me the subject of this research, and for his helpful and inspiring interest during the course of the experiments.

* See J. J. Thomson, 'Phil. Mag.,' vol. 11, p. 781, 1906.

The Charges on Positive and Negative Ions in Gases.

By JOHN S. TOWNSEND, F.R.S., Wykeham Professor of Physics, Oxford.

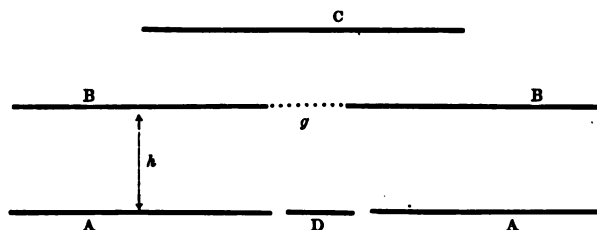
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In a paper on the Diffusion of Ions in Gases,* I described a method of comparing the charges on the ions generated in gases with the charge on an ion in a liquid electrolyte. If N be the number of molecules in a cubic centimetre of a gas at standard pressure and temperature, and e the charge on an ion, then $N \cdot e = 3 \cdot 10^8 \cdot U/K$, where U is the velocity of an ion in a field of unit electric force and K the coefficient of diffusion. Thus from separate determinations of the quantities U and K , the product $N \cdot e$ can be obtained.

If E is the charge on a monovalent ion in a liquid electrolyte, $N \cdot E = 1 \cdot 23 \times 10^{10}$, so that a comparison of the various charges may be made, and the calculations have shown that the charge on a positive or negative ion in a gas is nearly equal to the charge E . There were, however, considerable discrepancies, particularly with positive ions, which gave values of $N \cdot e$ as great as $1 \cdot 66 \times 10^{10}$ in some cases.

Some time ago, while examining these investigations, I found that, by a somewhat different method, it would be possible to arrange an experiment for determining $N \cdot e$ directly, and to arrive at much more accurate results than have been obtained hitherto.

In order to apply the principle, it is necessary to have the ions moving in a uniform field, and to find experimentally how they are distributed in some particular case. For this purpose two horizontal plates, A and B, were set at a distance h apart, and circular holes of the same radius were cut in the plates, the centres of the circles being in the same vertical line. A grating G of very fine wire was laid across the hole in the upper plate, and a metal disc D on an insulating support was fixed in the aperture of the lower plate, leaving a small air space between the disc and the plate, so that they should be insulated from each other.



* John S. Townsend, 'Phil. Trans.,' A, 1899, vol. 193.

The plate B was maintained at a potential V , and a third plate C above B was maintained at a potential V' greater than V and of the same sign. The lower plate and the disc were connected alternately to a sensitive electrometer, and during the course of an experiment their potentials did not differ appreciably from the zero.

The ions were generated in the air space between B and C by Röntgen rays, and positive or negative ions were driven to the grating according as the potential of C was positive or negative. The electric force being in the same direction above and below the grating, some of the ions pass through and travel under a constant electric force Z towards the central disc D. At the same time the ions diffuse laterally, so that some arrive on the disc and some on the plate. The greater the force Z the less time there will be for the diffusion, so the proportion of the total number that arrive at the disc increases with the force between A and B.

The ratio R of the number arriving at the disc to the total number was determined accurately with the aid of the electrometer.

The mathematical investigation of the distribution of the ions between the plates A and B can easily be made by considering the equations for the variation of the partial pressure p of the ions. The three equations corresponding to the three rectangular axes are of the form

$$\frac{1}{K} (pu) = -\frac{dp}{dx} + n \cdot X \cdot e,$$

where n is the number of ions per cubic centimetre (which is proportional to p), u the velocity and X the electric force along the axis of x .

Differentiating the three equations and substituting in the equation of continuity for the steady state,

$$\frac{d}{dx} (pu) + \frac{d}{dy} (pv) + \frac{d}{dz} (pw) = 0,$$

the following equation for p is obtained—

$$\frac{d^2p}{dx^2} + \frac{d^2p}{dy^2} + \frac{d^2p}{dz^2} = Ze \frac{dn}{dz} = \frac{N \cdot e \cdot Z}{P} \cdot \frac{dp}{dz},$$

where P is the pressure due to 760 mm. of mercury, at which pressure N is reckoned.

This latter equation shows that p at any point is a function of $(N \cdot e \cdot Z)$. The constants in the solution $p = f(N \cdot e \cdot Z)$ are functions of the position of the point and at the lower plate, where $z = h$, the ratio R may be obtained by integration. Thus $R = \int_0^a r p dr \div \int_0^b r p dr$, where r is the distance from the centre of the disc, a and b being the radii of the disc D and the plate B respectively.

Hence

$$R = \phi(N.e.Z).$$

It is not necessary to know the form of the function ϕ in order to see how to compare the charge on a positive ion with that on a negative ion, or to compare the charges on ions in different gases.

Experiments made with positive and negative ions for the same intensity of force Z gave a value of R for positive ions which was much greater than the value for negative ions. This shows that the charge on a positive ion is greater than the charge on a negative ion. The same value of R , within 1 per cent., was obtained for the two kinds of ions when the force used with negative ions was double that used with positive ions. Letting e_+ denote the charge on a positive ion and e_- the charge on a negative ion, then

$$\phi(N.e_+.Z) = \phi(N.e_- . 2Z)$$

for all values of Z .

Hence the charge on the positive ion is exactly double the charge on the negative ion. This shows that when a molecule of air is ionised by Röntgen rays, one positive ion and two negative ions are produced, the charge on the former being double that on either of the latter.

In order to find the absolute value of $N.e$, it is necessary to solve the differential equation in p . An exact solution can easily be obtained which satisfies all the surface conditions, since p can be expanded in a series of Bessel's functions. The distribution being symmetrical round the axis of z joining the centre of the grating with the centre of the disc, the differential equation reduces to the form—

$$\frac{d^2p}{dr^2} + \frac{1}{r} \frac{dp}{dr} + \frac{d^2p}{dz^2} = \frac{N.e.Z}{P} \frac{dp}{dz},$$

where r is the distance of a point from the axis.

Letting

$$p = q \cdot e^{-\theta^2 z},$$

the equation for q is

$$\frac{d^2q}{dr^2} + \frac{1}{r} \frac{dq}{dr} = \left(-\theta^2 \cdot \frac{N.e.Z}{P} - \theta^4 \right) q = -\lambda^2 q,$$

so that

$$q = J_0(\lambda r),$$

and

$$p = \sum \mu J_0(\lambda r) e^{-\theta^2 z}.$$

The values of μ and λ are determined from the surface conditions and θ^2 is the positive root of the equation

$$\theta^4 + \theta^2 \frac{N.e.Z}{P} = \lambda^4.$$

Hence p can be found at any point of the lower plate, where $z = h$, and

the integrations $\int_0^a pr dr$ and $\int_0^b pr dr$ can easily be obtained from the known properties of Bessel's functions. The connection between R and $N.e.Z$ was thus found, and a curve was drawn to show the values of R for a series of values of $N.e.Z$. When R is found experimentally the corresponding value of $N.e.Z$ can be found immediately from the curve. The expression for R in terms of $N.e.Z$ is very complicated and I have to acknowledge my indebtedness to Mr. C. E. Haselfoot in having assisted in making the necessary calculations from the tables of Bessel's functions.

I have made a number of determinations of R with different forces, pressures, and intensities of ionisation, and they all agree in giving results in accurate accordance with the theory. The values found for Ne are 2.41×10^{10} for positive ions and 1.23×10^{10} for negative ions. Each of these numbers represents the mean result of several different experiments in which none of the determinations differ from the mean value by more than 4 or 5 per cent., which shows that considerable accuracy can be obtained by this method.

When the value of $N.e$ is deduced by the first method which I gave,* the numbers corresponding to the positive ions were about 10 or 20 per cent. higher than those for the negative ions. Thus, when the rates of diffusion are compared with the velocities given by Zeleny,† the values of $N.e \times 10^{-10}$ for positive ions in air, oxygen, and hydrogen are 1.46, 1.63, and 1.63, and the corresponding numbers for the negative ions were 1.31, 1.36, 1.25. These numbers taken alone would not justify the conclusion that the molecules are ionised in the way that I have just found, but a little consideration shows that the relative values are of the kind that should be expected. If the effect of recombination be considered, it will be seen that a positive ion would rapidly combine with a negative ion when the charge on the former is $2e$, as the force between them is $2e^2$. After combining with one negative ion, the force between the positive ion and another negative ion would be e^2 , so that the second step towards complete recombination would not proceed so rapidly as the first. The result of this would be that after the positive and negative ions have been in the gas together for a short time, a large proportion of the positive ions would have one-half of their original charge.

The determinations of the coefficients of diffusion K were made with small ionisations that had been reduced by the process of recombination, and from a consideration of Zeleny's method of finding the velocities it is evident

* J. S. Townsend, *loc. cit.*

† 'Phil. Trans.' A, 1900, vol. 195.

that recombination must have been going on in his experiments also. Under these circumstances the numbers obtained for $N \cdot e$ by the first method correspond to positive ions, of which some have a charge $2e$ and others a charge e . The discrepancies from the value 1.23×10^{10} obtained for the negative ions are not greater than what might have arisen from experimental errors.

In the experiments I have just now made the recombination must have been negligible, so that no appreciable number of the positive charges could have been reduced from $2e$ to e .

A full description of the experimental methods used in these determinations will be given in a future paper, when the experiments which are in progress with different gases are completed.

On the Generation of a Luminous Glow in an Exhausted Receiver moving near an Electrostatic Field, and the Action of a Magnetic Field on the Glow so produced.

By FREDERICK JOHN JERVIS-SMITH, M.A. Oxon, F.R.S., University Lecturer in Practical Mechanics and Experimental Physics, Oxford.

(Received January 20,—Read January 30, 1908.)

1. In 1896* I found that bulbs exhausted as a Crookes radiometer, when bombarded by a discharge from a Tesla inductor, produced X-rays, and X-ray photographs of the hand were then made, using only exhausted bulbs having no terminals. The bulbs had the following dimensions: 5 cm. diameter, stem 12 cm. long, 0.4 cm. diameter.

I had from time to time noticed that when any of the exhausted bulbs were rubbed on the palm of the hand, they became luminous for a brief period while they were being rubbed.

In December, 1907, I returned to the subject, using these same exhausted bulbs in connection with certain apparatus in which plates of sulphur were employed as insulators. Happening to move an exhausted bulb near a sulphur plate in the dark, I noticed that it glowed for an instant. It then became evident that an exhausted vessel, moving in an electrostatic field, itself became electrified and consequently glowed.

2. An exhausted bulb was mounted by its stem in a hollow mandrel running in a bearing; it was rotated by means of a pulley, driven by a cord connecting it to a small motor. Under the bulb a plate of sulphur was placed in the horizontal plane at distances varying between 1 cm. and 13 cm. The glow was apparent at 13 cm.

3. The bulb was rotated about 20 times per second. The sulphur was rubbed on the hand before being placed below the bulb. When the bulb was rotated it became instantly filled with a luminous glow, with a patch of greenish light brighter than the rest of the glow situated about 90° from the vertical. When rotation was reversed, the patch appeared on the opposite side of the bulb, also about 90° from the vertical.

4. In the next experiment the statically charged body placed under the rotating bulb consisted of a brass disc supported on an insulated stem. The disc was connected to an electroscope, and charged to 1200 volts. The bulb was rotated as before; the charged disc remained charged during the

* 'Nature,' vol. 54, p. 594.

experiment, which lasted about six minutes, and showed no signs of being discharged.

5. An electrostatic field of opposite sign was maintained on two opposite sides of the bulb; the glow throughout the bulb was considerably increased, but when two similarly charged discs were placed at equal distances on the opposite sides of the bulb, the glow ceased, and when one was charged to a higher potential than the other the glow again appeared, apparently due to the difference of charge of the two discs.

6. Touching the rotating bulb lightly with a finger did not affect the appearance of the glow in any perceptible way.

7. The bulb was rotated in the electrostatic field due to the disc of sulphur which had been rubbed on the hand, placed above the bulb in the horizontal plane, and below the bulb an insulated metal disc was placed connected to the electroscope; no transfer of electricity to the disc was indicated.

8. A disc of sulphur (10 cm. diameter) was mounted on a face plate of wood rotated by a mandrel (running in ball bearings) as in a lathe; the disc of sulphur was rubbed so as to establish an electrostatic field. When it was rotated near an exhausted bulb or exhausted tube, no glow was produced.

9. The sulphur disc, while rotating if used as the inductor of an electrophorus, acted in exactly the same manner as if at rest. The disc was rotated from one revolution per second up to 20 revolutions per second.

10. Five bulbs were prepared and rotated in an electrostatic field of constant strength. Some were exhausted to the same condition of vacuum as the radiometer of Crookes; some to the condition of a Röntgen X-ray tube. The glow in those exhausted to the Röntgen vacuum was far brighter than that in those not so exhausted.

11. The electroscope used to measure the P.D. of the charges was designed by Professor Townsend, F.R.S., of Oxford; it is calibrated so that each division of the scale indicates 100 volts. It is capable of keeping its charge for many days.*

12. The experiments show that when an exhausted glass vessel is rotated in an electrostatic field an electrical glow is created, the intensity of which varies in some way with the velocity of rotation, while the position of maximum glow changes its position with the direction of rotation.

13. Since the bulbs were exhausted by means of a mercury pump (used by the manufacturer of Röntgen tubes), there may possibly be a very thin coating of mercury on the inner wall of the bulbs. An exceedingly minute

* 'Nature,' vol. 77, p. 149, "Sulphur as an Insulator," by F. J. J.-S.

coating of mercury on vessels exhausted by the mercury pump has recently been suggested as the cause of the change of conductivity of selenium when placed in a vessel exhausted by a mercury pump.*

The Action of a Magnetic Field on the Radiant Glow in an Exhausted Vessel rotated in an Electrostatic Field.

Considering the conditions subject to which the glow is generated it seemed probable that it would be unidirectional in its nature, and would therefore be acted on by a magnetic field. This was found to be the case.

In preliminary experiments on this point a permanent magnet was employed, but, for convenience of reversal of the poles, it was replaced by an electromagnet taken from a Morse instrument by Siemens and Halske. The poles of the electromagnet were placed within 0.5 cm. of the bulb, in several different positions.

The conditions of the experiment were varied in six ways:—

- (1) The static charge was either positive or negative.
- (2) The rotation of the bulb was either in the clock-hands sense or the reverse.
- (3) The magnetic pole, in different experiments, was north or south.

Both a horseshoe electromagnet and a long cylindrical electromagnet were used in the different experiments: the current of electricity used to energise the electromagnet was supplied from accumulators, a reversing key being placed in the circuit.

Effect of two magnetic poles on the glow. (Fig. 1.) D, disc giving the electrostatic field, charged inductively by means of a disc of sulphur rubbed on the dry hand.

Rotation of the bulb, clock-hands sense, to an eye at A. Revolutions 20 per second.

No current on electromagnet. A greenish-blue glow filled the bulb.

Electromagnet on, the glow took the form of an equatorial bright band, brightest between the poles of the electromagnet, where its shape was modified as shown.

Fig. 2.—Bulb exposed to south pole. Charge on D as in Fig. 1. Rotation, clock-hands sense. The glow filled a hemisphere of the bulb P with an equatorial band a little more brilliant than the rest of the hemisphere.

Fig. 3.—Bulb exposed to south pole. Rotation contrary to clock-hands. The glow filled a hemisphere of the bulb Q with equatorial band a little more brilliant than the rest of the hemisphere.

If, while the charge on D and the rotation of the bulb are kept the same,

* 'Nature,' vol. 77, p. 222.

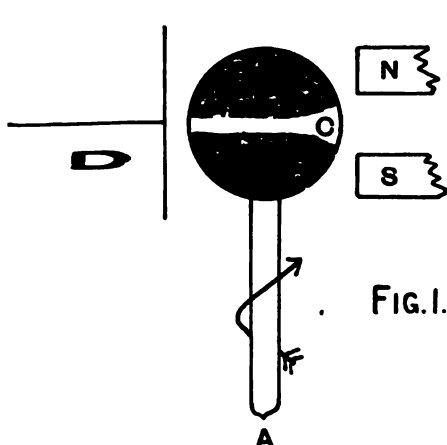


FIG. 1.

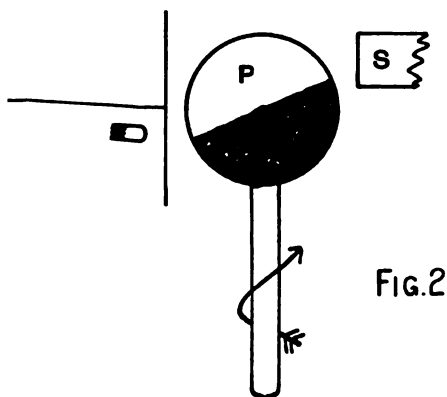


FIG. 2

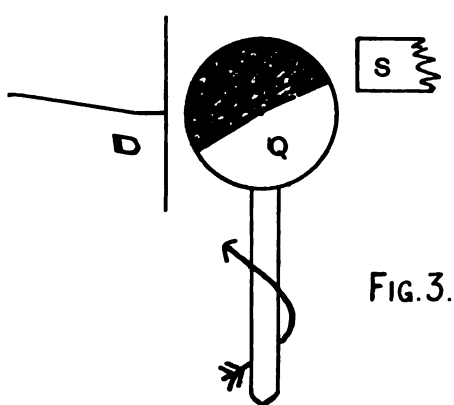


FIG. 3.

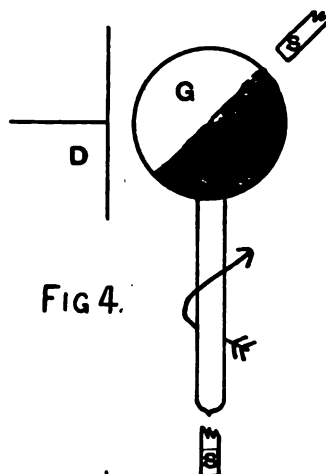


FIG 4.

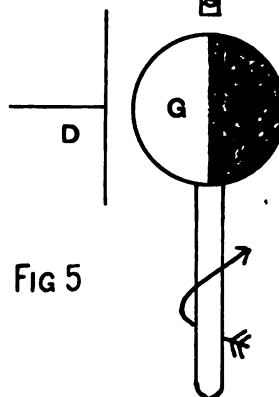


FIG 5

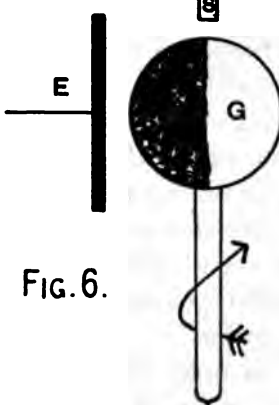


FIG. 6.

the magnetic pole is changed, the glow phenomenon is reversed. Also when the charge on D and the magnetic pole are kept the same, but the sense of rotation is reversed, the glow phenomenon is reversed.

14. The experiments in which one pole of the horseshoe magnet was employed were all repeated with an electromagnet of cylindrical form, so that only one pole was near the bulb.

Fig. 4.—The electrostatic field was maintained by a brass disc D charged by induction from rubbed sulphur. The views of the apparatus and phenomena are as seen by an eye above looking vertically down on them.

The axis of the electromagnet was placed in the horizontal plane through the centre of the bulb, at 45° from the axis of rotation of the bulb. Glow in hemisphere G. Reversal of the magnetic pole deflected the glow to the opposite hemisphere. Rotation, clock-hands sense.

Fig. 5.—The axis of the electromagnet was in the axis of rotation of the bulb. Magnetic pole south. Glow G in hemisphere nearest to the disc. This was exactly reversed when the north pole was used.

Fig. 6.—E, a sulphur disc which had been rubbed, was used to maintain the electrostatic field. Glow at G, away from sulphur disc. Magnet pole south. — The glow illuminated the opposite hemisphere when the north pole was presented to the bulb.

In each case the glow is most brilliant in a region the mid-point of which is about 90° from the axis of the electromagnet.

Shifting the pole of the electromagnet shifts the equatorial plane separating the dark and glow-filled hemispheres.

15. A summary of the relationship which exists between the direction of rotation of the bulb, the charge of the inductor D, and the name of the magnetic pole, may be stated thus.

When the rotation of the bulb is in the clock-hands sense, to an eye looking along XO, the charge on the inductor positive, the magnet pole south, the deflection of the glow is to the right of the south pole as shown in fig. 7. B, bulb with axis of stem lying in OX, magnet pole south, Pp direction of deflection of glow matter. If any one of the conditions, namely, sense of rotation, sign of charge on the inductor or magnet pole, be reversed, while the other two remain unchanged, the deflection of the glow is reversed.

16. Experiments have been made and are now being continued with a view to discover whether the glow will affect a photographic plate. When placed in a light-tight case, only very slight traces of this action have as yet been found by me.

17. In order that the phenomena might be seen under any climatic conditions, the whole of the inductual apparatus was enclosed in a box having a glass lid, fitted with an air-tight rubber joint, the interior being kept dry with sulphuric acid.

The discs were charged from the outside of the box by means of conductors

led into it through sulphur plugs. The phenomena could then be observed for any required time.

18. Many forms of exhausted vessels were employed; of these an exhausted ring (10 cm. diameter, made from tube having an internal bore of 1 cm.)

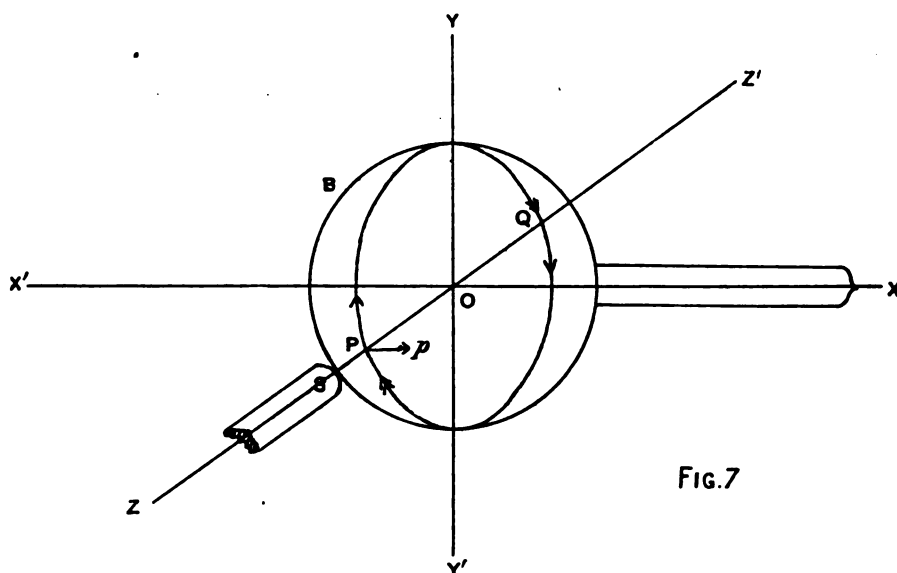


FIG.7

revolving about a diameter, in an electrostatic field, gives a good and beautiful glow.

19. In conclusion, I wish to offer my best thanks to the President of the Royal Society for comments on the phenomena described in this paper.

The diagrams for the paper were prepared by Mr. E. J. Jarvis-Smith, R.F.A., who has assisted me in carrying out the experiments.

The Spectrum of Magnesium and of the So-called Magnesium Hydride, as obtained by Spark Discharges under Reduced Pressure.

By E. E. BROOKS, B.Sc., A.M.I.E.E.

(Communicated by Sir William Crookes, F.R.S. Received October 14,—Read December 12, 1907.)

In 1878 Liveing and Dewar* examined the spark spectrum of magnesium in an atmosphere of hydrogen and noticed a bright line of wave-length about 5210, occasionally accompanied by other fine lines on the more refrangible side. In later papers† they remark that this line is only visible in hydrogen or when the C and F lines are also visible, and describe more fully the “two sets of flutings and a pair of fainter bands” which accompany it, and which appear to have been independently discovered by Ciamician.‡ Liveing and Dewar inferred that some compound of the metal and hydrogen was formed, and since the time of their research these lines and flutings have been known provisionally as the “hydride” spectrum.

The term will be retained for convenience, but it must be understood that its correctness is not assumed.

Numerous researches have since been made to elucidate the relations between the arc and spark spectra of magnesium, partly in connection with the mechanism of electric discharges in general and partly on account of the importance of the line 4481 in astrophysics and the question as to whether its intensity in stellar spectra can be taken as a criterion of temperature. Of especial interest are the observations of Crew, Basquin and others as to the effect of a hydrogen atmosphere on the arc spectrum of this and other metals. The results obtained cannot be briefly summarised, but references are appended to the more important work dealing with the subject.

Very little attention, however, appears to have been given to the hydride spectrum, which is a highly complex system of bands and flutings extending over the whole range of the visible spectrum, from the hydrogen C line to the magnesium triplet at 3830.

The writer's experiments were suggested by phenomena met with in the course of a research on the spectra produced when compound bodies are used as electrodes *in vacuo*. The discharge vessel was usually a lamp glass fitted

* ‘Roy. Soc. Proc.’ vol. 27, p. 494.

† ‘Roy. Soc. Proc.’ vol. 30, p. 94 ; vol. 32, p. 197.

‡ ‘Sitzber. Akad. Wissensch.’ Wien, 1880, p. 437

with rubber stoppers carrying the electrodes, and the pressures employed varied from atmospheric to 1 or 2 mm. of mercury. A large number of observations, extending over several years, were made in different gases and with different kinds of discharge, but in this paper only the results obtained in the two special cases of alternating currents of high and low frequency will be dealt with.

For high frequencies a spark coil was shunted with two large Leyden jars of total capacity about 0.004 microfarad, and an adjustable spark gap was put in series with the discharge vessel. The primary current was from 10 to 16 amperes as a rule, obtained from alternating mains at frequency 50, no contact breaker being employed. The electrodes usually consisted of two long spirals made from single strips of thin commercial magnesium ribbon, enclosed in glass jacketing tubes with from $\frac{1}{2}$ to $\frac{3}{4}$ inch projecting at the ends and about $\frac{1}{2}$ inch apart; this form being adopted because a simple device enabled them to be fed forwards or backwards as required without impairing the vacuum. Absolute gas-tightness was of course impossible, but the rate of leakage could be made quite small.

At a pressure of from $\frac{1}{8}$ to $\frac{1}{4}$ inch of mercury and with an auxiliary spark gap of from $\frac{1}{16}$ to $\frac{1}{8}$ inch in length, an oscillatory discharge passes through the apparatus whose R.M.S. value (as read on a hot wire ammeter) is about 3 amperes, which implies a maximum value of the order of 100 or 200 amperes. The discharge then assumes one of two possible forms which are essentially the same in all gases tried. If the electrodes are too massive or too far apart, there is a luminous gas column between them and they are surrounded by green ragged haloes which do not tend to extend into the gas column. This state may persist indefinitely without any marked waste of the electrodes or deposit on the walls of the vessel, and the spectrum is a mixture of gaseous and magnesium lines. In the case of hydrogen, C and F are especially intense. Increasing the pressure to 3 or 4 inches of mercury does not much affect the metal lines, but makes the four chief hydrogen lines very broad and diffuse (the C line, however, often being much sharper than the others).

If the electrodes are not too massive, *i.e.*, if they are the single spirals of ribbon already mentioned, this discharge quickly passes into a new and more interesting form. The green glow increases in size and brilliancy, and becomes a green flame enveloping the electrodes and bridging across the whole distance between them, under favourable conditions completely replacing the gas column. The magnesium ions have become the carriers of the discharge, and the arrangement is analogous to a mercury lamp in which the mercury is replaced by magnesium. This state is perhaps most readily

obtained in hydrogen, and in this gas the phenomena are least complicated by secondary actions. At the instant it sets in, a fine black deposit of metallic magnesium begins to form on the walls of the vessel, and rapidly obscuring the view, although by various devices observations can be maintained as long as is necessary. Meanwhile, the thin electrodes waste quite slowly away, neither fusing nor softening, and a slow absorption of gas goes on, so that a few bubbles must be admitted now and then in order to keep the vacuum from becoming too good and interfering with the oscillations. This will be called the "high-frequency flame discharge." It gives a brilliant spectrum of perfectly definite character, which can be recognised at a glance, and which differs in many respects from the spark spectrum at ordinary pressures, and also from the normal arc spectrum, but bears some resemblance to the arc spectrum under reduced pressure, as described by other investigators.

The points of chief importance may be summarised as follows (assuming at first hydrogen to be present):—

(1) A good magnesium spectrum is obtained, in which the gas lines are not obtrusive, although the C and F lines are sharp and strong and the fine line hydrogen spectrum more or less visible at the red end. The metal line 4481 is very intense, but still sharp and clear. As regards the fainter magnesium lines, one at 3938 is always found on negatives taken with sufficient exposure, and there are two very faint lines near 3895 and 3900, and another pair near 3848 and 3853. These appear to correspond to some of the fainter lines of the spark spectrum at ordinary pressures (excepting the stronger line 3938, which seems to be only mentioned by Fowler and Payn).^{*} Two other faint lines at 3944 and 3961 may be due to aluminium as impurity. (These results were obtained with glass prisms, and observations have not as yet been extended into the ultra violet.)

(2) In hydrogen the hydride spectrum is always present in great intensity. This is, in fact, the most convenient method of obtaining it. It is usually present, often with almost equal intensity, in the case of other gases, unless very special precautions are taken to exclude water vapour, but disappears in the complete absence of hydrogen and water vapour.

(3) A very prominent feature is the presence of two pairs of sharp lines at wave-lengths approximately 4433·6, 4428·2, 4390, 4385, the more refrangible pair being slightly the stronger. This is the only type of discharge which gives them readily. Three of these lines appear to have been first observed, but not identified, by R. A. Porter.[†]

^{*} 'Roy. Soc. Proc.', 1903, vol. 72, p. 253.

[†] 'Astrophysical Journal,' 1902, vol. 15, p. 274.

Fowler and Payn* observed both pairs in the spectrum of the magnesium arc in an air vacuum, and concluded that they were really enhanced lines of the metal. No other reference to them has been found, although they are visible in a reproduction of the magnesium arc spectrum *in vacuo*, accompanying a paper by J. Barnes.† As these lines will be frequently mentioned, it will be convenient to term them the "F and P" lines. Their frequency difference is about 27, a number bearing a simple relation to the frequency differences of 40·5 and 81, which hold good respectively for two pairs and three pairs of magnesium lines in the ultra violet.‡

The high-frequency flame discharge can be produced in a coal gas, air, nitrogen, or carbon dioxide vacuum (these being the only gases tried), providing the terminals are not too massive. A very great momentary current density appears to be an essential condition. The type of spectrum just described remains the same, and, under ordinary conditions, the hydride flutings and the C and F lines of hydrogen are invariably present, often with intensity little inferior to that obtained in hydrogen, so that photographs of the discharge in air or in hydrogen are practically identical. As already stated, this is due to the presence of a trace of water-vapour, extremely difficult to get rid of. Eventually it was eliminated by placing phosphoric anhydride within the discharge vessel itself for each experiment, and then, in the complete absence of hydrogen or water-vapour, no hydride spectrum appears.

In a coal-gas vacuum the carbon fluting at 4315 comes out strongly. In an air vacuum the first effect is a rapid fusion and scattering of the electrodes, due to the oxygen present, but the action quickly subsides, and the true flame discharge sets in with slow subsequent waste. This effect is still more pronounced in carbon dioxide. In nitrogen the discharge presents the usual features, but it is difficult to keep it steady for any length of time, and there is a strong tendency for a red nitrogen glow to appear at one of the electrodes.

In all gases absorption occurs during this kind of discharge.

The low-frequency discharge (*i.e.*, without jars) is quite different in character and in spectrum. In this case it was desirable to have at command a stronger current than could be obtained from a spark coil, and hence a small 2000-volt transformer, fed from alternating mains at frequency 50, and with an adjustable liquid resistance in the secondary circuit, was usually employed, also magnesium rods about 3/16 inch diameter were

* 'Roy. Soc. Proc.,' 1903, vol. 72, p. 253.

† 'Astrophysical Journal,' 1905, vol. 21, p. 75.

‡ Baly, 'Spectroscopy,' p. 502.

more convenient to manage than strip, for the electrodes fused with a current whose R.M.S. value was perhaps only one-tenth of that carried easily under the former conditions. For a long time the results obtained were very puzzling, the "F and P" lines and the hydride spectrum appearing or disappearing under apparently identical conditions, but whilst the latter was more often present than not, the former were very seldom found on the negatives. Eventually it became apparent that several distinct spectra were present, the facts observed being briefly as follows.

When a current of, say, 0.3 or 0.4 ampere is passed through rod electrodes in a hydrogen vacuum at about 2 or 3 cm. pressure (the vessel itself containing phosphoric anhydride), the first effect is a perfectly steady pale glow around each electrode, which gives a faint hydrogen spectrum, but there is no luminous gas column between them. If no special care has been taken with the electrodes, *i.e.*, if the surfaces are oxidised, vivid green points may keep flashing out on them, most numerous at first and gradually diminishing as time goes on. The spectrum of these points has been observed frequently, and also photographed. It is characterised by the presence of the hydride flutings and the "F and P" lines, and the great strength of the line 4481, but differs from the high-frequency flame spectrum in the comparative weakness of the minor magnesium lines.

If the electrodes be trued up in a lathe so that their whole surface is perfectly bright and clean, very few or no flickering green points are seen, and in any case they disappear more or less completely in a very short time, but when one does flash out, its characteristic spectrum flashes out with it. The subsequent course of events is practically the same whether the rods are clean or not. Gradually a pale green tint creeps into the perfectly steady halo surrounding each electrode. This gives the *b* triplet and the line 5528 on a background of the two hydrogen spectra, but there is not a trace of the hydride flutings or of the "F and P" lines, 4481 being very faint and the other magnesium lines practically invisible. This spectrum has been repeatedly photographed, but only the brighter lines are shown.

The green tint steadily increases in intensity until finally, with the suddenness of switching on a lamp, the discharge lights up brilliantly, the glow around the electrodes becomes intense, producing a flame effect not unlike that already described (but really quite different in structure and properties), and accompanied by a rapid and copious evolution of brownish-black fumes.* With equal suddenness the gaseous lines disappear completely,

* This stage marks the fusing point of the electrodes. Later experiments with unidirectional current have shown that the green glow and subsequent phenomena occur only at the cathode.

leaving an intensely bright and sharp magnesium spectrum, but without the hydride flutings and without the "F and P" lines. The line 4481 is distinct and about equal in intensity to 4571, and relatively much fainter than 4703 and 4352.

It is difficult to eliminate completely the hydride spectrum, but when it appears it is in flashes, and in any case its intensity is very small compared with its great strength in air or nitrogen not specially dried. Photographs show barely a trace of it.

Hence the mere presence of *dry* hydrogen is not sufficient to bring out the hydride flutings.

In one experiment, without disturbing the apparatus, the connections were then changed to the coil with jars and the high-frequency discharge passed. As is usual with such thick electrodes, the flame state was not obtained, and although the "F and P" lines were well seen the hydride flutings were invisible, except that after long running a faint trace of the line 5210 appeared. In another experiment of the same kind some approach to the true flame discharge was obtained for a few moments and then the hydride flutings appeared distinctly, but only during that time. The general inference is (since abundantly confirmed) that the "F and P" lines are not in any way related to the hydride spectrum; they are probably true magnesium lines, but require the jars to bring them out well, whereas either at high or low frequency the hydride flutings require something more than the mere presence of hydrogen.

Unless special precautions are taken to eliminate water-vapour, the low-frequency flame discharge in hydrogen always gives a strong hydride spectrum, but the "F and P" lines have never been observed in it, although carefully looked for. For instance, rod electrodes which had been used to demonstrate the absence of the hydride spectrum in dry hydrogen were directly afterwards placed in another vessel, but *without* phosphoric anhydride. This vessel was then well washed out with hydrogen (passed through strong sulphuric acid and over phosphoric anhydride before entrance), but when the final state set in the hydride spectrum appeared steadily.

Hence this spectrum can be seen in the presence of a trace of water-vapour under conditions in which it would be totally absent without that vapour, a hydrogen atmosphere being present in both cases.

A larger quantity of water-vapour makes very little difference, merely bringing out the oxide fluting at 5007.

Such results made it a possible hypothesis that the hydride bands were always connected with the presence of oxide or water-vapour, in which

event there would be no occasion to assume the existence of a "hydride" at all. It would simply be the spectrum of the metal in a peculiar and nascent state. Some important evidence in this direction had been obtained years previously in the case of other elements and compounds. For instance, in a similar way, but with more difficulty, a jet-like glow can be obtained from point sources on an aluminium electrode, and this always gives the characteristic fluting spectrum of that metal, by some writers attributed to the oxide; but Hemsalech has supported Aron's view that it is really due to the element itself. It was, however, found that the hydride spectrum appeared with great intensity in the high-frequency flame discharge in hydrogen even when every effort was made to eliminate oxide and water-vapour. It is always difficult to estimate how far such efforts have been successful, but apparently there are two distinct methods of producing the state or substance which gives this spectrum, one dependent on a chemical change accompanying ionisation and the other on ionisation by a current of very high maximum value.

The low-frequency discharge in dry air or nitrogen presents problems of more difficulty and is still under investigation. It is, however, perfectly certain that there are at least two quite different spectra to be seen in one and the same discharge, having distinct and recognisable sources. One of these is characterised by the intensity of the line 4481; 4703 is weak and 4571 invisible, and the hydride spectrum is absent. In air the oxide fluting at 5007 is strong at first, disappearing later, and in nitrogen it is absent. The other spectrum, which depends in some way on the presence of nitrogen, probably on the formation of nitride, is remarkable on account of the great intensity of the line 4571, which, next to the *b* triplet, is by far the strongest line in it, 4481 being usually invisible, 5711 faint, and 5528 and 4703 of only moderate strength. When the air or nitrogen has not been specially dried the hydride spectrum appears with great brilliancy. There is an initial stage in which the cathode gets hot and may fuse, even with small current, but if "nursed" through this, a current of from 1 to 2 amperes may be passed for an indefinite time without fusion. The "F and P" lines are faint, but in all cases are seen when discharge is sufficiently intense. It is hoped to deal more fully with this part of the work in a later paper.

As regards the long-debated question as to whether the intensity of the line 4481 is a criterion of temperature, it may be pointed out that in the high-frequency flame discharge the single spiral of thin magnesium ribbon never fuses, although it is carrying a considerable current, its temperature probably being kept down by the free ionisation going on. Yet this is the discharge which gives the line 4481 with the greatest intensity and sharp-

ness. In the low-frequency discharge the whole apparatus is much hotter and the electrodes readily fuse. In fact, this latter spectrum has been photographed when the thick electrodes have been in a molten state and liquid globules dropping from them, without any marked increase in the intensity of this line, which is relatively weak in this kind of discharge, and, under these conditions, the spectrum as a whole is not so good as when the same state occurs without fusion.

Observations were made in several different ways on the high-frequency discharge, in order to determine the relation of the various lines to the electrodes. In some experiments a three-way globe was arranged so that one of the electrodes could be seen "end on," the other electrode being a ring of iron wire. An image of the former electrode was thrown on the slit of a spectroscope by means of a lens, and thus different parts of the glow examined. The line 4481 was only conspicuous quite close to the electrode, a slight displacement suddenly cutting it off, as was also the case with the hydride bands. The line 4703 remained visible a little longer than 4481, whilst the *b* triplet was brilliantly visible long after the latter disappeared, and, in fact, could always be seen more or less clearly in any part of the globe. The line 5528 varied with the *b* triplet—a fact often noticed—as if these lines have a common origin or are connected in some way.

The discharge was also photographed by means of an ordinary camera with a diffraction grating in front of the lens, but without a slit. The negatives showed the 4481 light locally strong at the electrodes, whilst an image of the whole lamp glass was formed by the light of the *b* triplet, and also, but more faintly, by the light of the violet triplet at 3830. Hence this latter radiation pervades the whole space as does that of the *b* group—due mainly perhaps to reflection—but partly to a real luminescence at considerable distances from the discharge proper. Similar results were obtained by using an ordinary prism spectrograph without a slit, and the phenomena can be observed directly in a specially clear and interesting way by means of Dr. Marshall Watts' "Binocular" spectroscope. The 4481 light can be seen flickering brightly close to each electrode, and with a small gap and a strong discharge extending faintly across it. The whole globe is seen in the light of the *b* group, and also in the light of the yellow line 5528, these flickering in unison.

These observations are merely given as confirmatory of results obtained by other investigators. It may, however, be remarked that the locus of the line 4481 is visible without any apparatus at all. In the true high-frequency flame discharge the green glow envelopes the electrodes and

bridges over the space between them, but the root of the discharge is distinctly blue, and it is this blue region which gives the 4481 line most strongly. (The low-frequency flame has no such blue core.) The "F and P" lines were not examined in the same way, but in all probability it will be found that their source lies even closer to the electrodes.

Some useful information as to the relation between the various phenomena already described and the sign of the electrodes was obtained by separating the components of the current in a magnetic field. For this purpose a narrow lamp glass was generally used, placed horizontally between the poles of an electromagnet so that the discharge was at right angles to the field, the magnesium electrodes being bifurcated so that on each the locus of origin of a positive and negative discharge could be readily seen. Sometimes one of the electrodes was an iron ring. With the means available the experiments were somewhat troublesome, and it has not been possible to obtain a direct current of sufficient voltage to confirm the results, which all pointed to the same conclusion.

The high-frequency discharge separated into two paths, equally pervaded by the green flame, and the faint bluish root which gives the 4481 line was found to be on the positive source only. Blackening took place by diffusion uniformly all round the tube, no localisation being noticed.

When the low-frequency flame was used, each electrode showed a bright green glow,* also attached to the positive source, but without a blue core. In this case the blackening was markedly local; the glows behaved much more like jets, and could be driven in any predetermined direction by the field, instant blackening occurring in exactly that direction. The experiments were decisive as to the positively charged character of the magnesium ions. When one electrode was of iron, this also possessed a green positive glow, and by the same method it was found that positively charged magnesium ions were returning from it. The pressure used was about 2 inches. These experiments were made in hydrogen, but a remark occurs in a notebook, made nearly three years since, to the effect that "the green glow, due to incipient combustion in an air vacuum, clearly and definitely follows the field, always being on the anode, and accompanied by brilliant whitish points." (These points are due to incandescent oxide.)

It was much more difficult to study the cathode by this method, and certain curious results obtained lack confirmation and are being investigated further. In one experiment, also made long ago, a three-way globe was

* This refers to a particular stage in the discharge. The facts are somewhat complicated and are being examined further, but the green jets always act like positively charged streams.

used, fitted with a third idle terminal, a small metal disc which could be kept charged positively or negatively by a Wimshurst machine whilst the discharge was passing. This was of the high-frequency flame type, and it was found that when the disc was kept positive, no black deposit formed on it, whereas when it was negative, such a deposit formed on it as well as on the walls of the globe. If the third terminal was quite close to the discharge column, the black deposit formed upon it in either case.

Apart from the question of charge, there are certain well-marked peculiarities in the evolution of fumes and formation of deposits which seem worthy of brief mention. It has already been stated that when the high-frequency flame discharge occurs in the presence of a trace of oxygen, there is an initial stage of fusion during which small particles of metal may be projected in various directions. These strike the glass at various angles, either rebounding or adhering as small metallic spheres flattened by the impact, and would not have attracted attention except for a peculiar structure invariably present in the splash. The metal particle is surrounded by a dark ring, and outside this, at a greater distance, is another fainter ring, as if the flying particle was surrounded by an atmosphere much larger than itself. According to the direction of impact, these rings may be nearly circular or portions of ellipses. When a particle strikes at almost grazing incidence, it leaves a long trace broken up into a series of separate splashes, but on either side is always found the faint line which marks the boundary of this atmosphere. The particles themselves may average a millimetre or so in diameter, the largest met with being 5 mm. and its "atmosphere" 2 cm. in diameter.

The fumes from the low-frequency flame discharge are usually lighter coloured, more distinctly visible, and form in a quite different manner. The projectile effect is very seldom met with, but instead one frequently obtains, especially in air or nitrogen, very large and remarkable spiral formations on the glass, which, under favourable conditions, may be seen to correspond to almost stationary whirls inside. Single instances of this kind would not be noteworthy, but it is remarkable that when such formations occur at all they are always of exactly the same type, and their probable appearance or otherwise can be predicted in advance.

[*Note added January 25th, 1908.*—Since this paper was written, Professor Fowler has shown that the hydride bands and flutings occur in the spectra of sun-spots; a most interesting and important discovery; and he remarks that "there need be no hesitation in attributing the flutings in question to the compound magnesium hydride."* It is, however, somewhat difficult to

* 'Notices Roy. Astron. Soc.,' vol. 67, No. 8, p. 530.

imagine a compound of the metallic hydride type existing as such in the sun, even at the relatively low temperature of a sun-spot; but, assuming this to be the case, and also that it is really formed in the arc and spark, it is still more difficult to understand why it eludes isolation by chemical means. One would naturally expect magnesium hydride to be an unstable compound, and apparently the only chemical evidence for its existence is to be found in a paper by Winkler,* who obtained a non-homogeneous substance (by heating a mixture of Mg and MgO to redness for four hours in an atmosphere of hydrogen), which certainly appears to have contained hydrogen, but whose exact composition seems somewhat doubtful.

On the other hand, in the current number of 'Nature'† is a paragraph referring to an article in the 'Observatory,'‡ by Father Cortie, who has many times recorded lines attributed to water-vapour in the spectra of sun-spots, and who suggests the possibility of the presence of superheated steam. Again, it may be noted that the metallic banded spectra of which the hydride flutings are merely one instance, are especially readily obtained in the oxyhydrogen flame, and Hartley and Ramage attribute these to the metal itself. Professor Fowler (whom I find has also been working for some years at the hydride spectrum) informs me that the most convenient way of producing such spectra is in the "flame" of the electric arc, but from my own experience I have no difficulty in believing that amply sufficient water-vapour may be present in this case also, unless very special precautions are taken to ensure its absence. On the whole, it seems best to regard the objective existence of the hydride as an open question, awaiting further experimental evidence.]

REFERENCES TO PREVIOUS WORK BEARING ON THE MAGNESIUM SPECTRUM.

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† January 23, 1908, p. 281.

‡ January, No. 392, p. 51.

Notes on the Application of Low Temperatures to some Chemical Problems: (1) Use of Charcoal in Vapour Density Determination; (2) Rotatory Power of Organic Substances.

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(Received February 6,—Read February 20, 1908.)

(1) Use of Charcoal in Vapour Density Determination.

In a recent paper* Barkla and Sadler describe the investigation of the penetrating power of the secondary Röntgen rays emitted by different elements, which they find to be dependent on the atomic weight of the element. The behaviour of nickel was found by those investigators to be abnormal, and could only be reconciled with the behaviour of other elements by assigning to nickel an atomic weight of 61.4, a value considerably higher than the accepted value, 58.7.

We therefore considered it of interest to make some further determinations of the density of nickel carbonyl at low pressures (when it would approximately obey the gas laws) by the use of a new method of manipulation which enables greater volumes of vapour to be employed, while, at the same time, the accuracy of the weight of the nickel carbonyl used in each experiment was considerably improved.

Previous determinations made by us† gave the value 83.3 at 63° C. and 760 mm. (when slight dissociation had taken place) and 85.6 at 17° C. and 67.7 mm., when no dissociation could be detected. These results show no indication that the accepted atomic weight of nickel is too low.

The basis of the present method is the use of charcoal at low temperatures to absorb gases and vapours. As liquid air is the material used for cooling, easily condensable vapours would, at the low temperature, have such a small tension that even the charcoal might be dispensed with, so far as one of the operations is concerned; but as its presence was not a disadvantage, it was retained in all the condensers.

In the following experiments, the vapour or gas, of which the density had to be determined, occupied a definite known volume at 0° C. under a measured pressure, and was absorbed in a small bulb filled with charcoal cooled in

* 'Phil. Mag.,' 1907, vol. 14, p. 408.

† 'Roy. Soc. Proc.,' 1903, vol. 71, p. 427.

liquid air which was afterwards weighed. In the conduct of the several operations it was found most advantageous to use three charcoal reservoirs for the purposes of air exhaustion and condensation.

The apparatus is sketched diagrammatically in fig. 1, and the following brief general description of it, and the mode of procedure, will make clear the essential details of the method.

A is a flask whose volume is about 2 litres, which is connected to a mercury manometer at B, and through a stopcock at C, to a weighed bulb F, with separate stopcock containing cocoanut charcoal. A stopcock at D enables communication to be made to a suitable reservoir containing the substance whose vapour density was to be determined, or to any gas generating mixture like that used for the production of carbonic acid. As all air has to be removed and a high vacuum reached in this part of the apparatus, it is convenient to seal on a special charcoal condenser, not shown in the drawing, instead of exhausting the whole apparatus by means of the one charcoal reservoir. During the charcoal exhaustion, liquid substances, like nickel carbonyl, ether, or sulphurous acid, were frozen at the temperature of liquid air. The usual preliminary washing out of the flask by the gas or vapour under examination made no detectable difference in the densities. The volume of the flask A and the connecting tubes enclosed between the stopcocks C, D, and a mark at B on the manometer tube, was ascertained from the weight of water at 0° C., which filled the space and was found to be 2161.6 c.c. The contraction of the flask, when the internal pressure was reduced to 40 mm., was found to be approximately 1 c.c. Taking the weight of air displaced by the flask as 2.58 grammes, we get the value 2163.2 c.c. as the volume of the exhausted flask.

This gas or vapour receptacle, after charcoal exhaustion, was surrounded with melting ice, all except a small portion of the manometer tube at B, which had to be left uncovered in order to take readings of the level of the mercury. The volume of the exposed part was, however, not more than 2 c.c., so that the error introduced by this, being at a temperature above 0° C., is negligible.

Beyond the tap C the apparatus is connected through a tube G to a bulb H containing cocoanut charcoal, and by a side tube to a Fleuss pump, also by another side tube with a stopcock J to a small bulb E containing charcoal. The weighted bulb F, also containing charcoal, was connected to the rest of the apparatus by a piece of thick rubber tubing, so that it could be detached and weighed. This rubber joint in refined experiments might be replaced by one of ground glass.

The mercury reservoir below the manometer B was movable, so that the

upper surface of the mercury could always be brought approximately to the level of the mark on B and carefully adjusted by means of a plunger in the reservoir. The stopcocks were all carefully selected, and after proper lubrication were found to allow no appreciable leak into the exhausted apparatus on standing for many days.

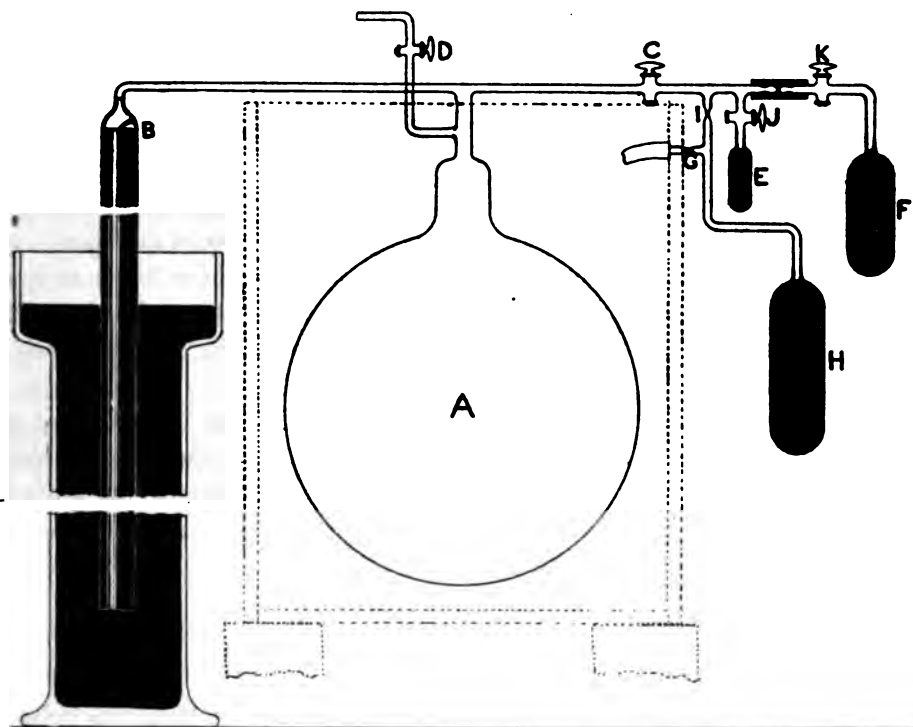


FIG. 1.

The arrangements for supplying the vapour were varied according to the substance used, and will be described in each case. The stopcock D being closed, C, J, and K open, the whole apparatus was exhausted through the side tube at G by means of a Fleuss pump, while the three charcoal bulbs were heated by means of a Bunsen burner. The side tube was then sealed off at G, and the bulb H inverted in liquid air for several hours, usually over night, after which the tube at I was fused and the charcoal condenser removed. The vacuum left is less than a ten-millionth of an atmosphere. During the main period of the charcoal exhaustion of the whole apparatus the stopcocks J and K were closed. The flask being now shut off by closing the stopcock C, the charcoal bulb F was detached, weighed with an equal volume counterpoise, and again connected to the

apparatus. The small space in the connecting tubes between C and the taps J and K was now necessarily filled with air, which was removed by immersing the bulb E in liquid air for about 10 minutes, and then shutting stopcock J.

Meanwhile the 2-litre flask A was surrounded with powdered ice, and the height of the mercury column in the manometer determined by means of a cathetometer. It is evident that the accuracy of the results will depend on the determination of pressure, since the errors here will be greater than those in the determination of the volume of A or of the weight of the vapour.

The cathetometers used (one of which was very kindly lent by the Cambridge Scientific Instrument Company) were capable of reading to 0.02 mm. Four readings of each surface of the mercury were taken, the condition of lighting and background having previously been arranged so as to ensure the best result obtainable, and the mean of these to the nearest tenth of a millimetre taken, this being sufficiently accurate for the main object in view, namely, to see if the atomic weight of nickel was considerably higher than 58.7.

The gas or vapour was now introduced through the tap D to any desired pressure, D was closed, and after adjusting the level of the upper surface of the mercury to the mark on B, the pressure was again determined. Several determinations of the pressure were usually made, but it was found that equilibrium was very soon reached, and after about 10 minutes the pressure did not change.

When the charcoal bulb F is immersed in liquid air, the taps C and K being open, the vapour in A is rapidly condensed in F. The exhaustion of the vapour from the flask was allowed to go on for about one hour, though in most cases no measurable diminution of pressure could be detected after about 10 minutes cooling. The taps C and K were then closed, F was detached and weighed against an exactly similar counterpoise after the expiration of a sufficient interval for it to acquire the atmospheric temperature. The flask is now left exhausted and ready to be recharged with vapour or gas, and another determination made. It was found advisable to exhaust and heat the charcoal in F after each experiment.

The weight of vapour filling A at 0° C. and under a measured pressure is thus determined, from which the vapour density can be calculated.

One difficulty with regard to the determination of the pressure must be noted. The pressure of the vapour is found from the difference in the readings of the mercury manometer taken at different times. During the interval between these readings the atmospheric pressure may change, and it was found in certain cases that owing to this cause the initial and final

readings of the manometer did not agree. When this is observed the pressure of the vapour is best obtained from the difference between the reading of the manometer before and after introducing the vapour, since the interval between these readings is not long, usually about half an hour.

In order to test the method, some condensible gases, whose vapour densities are accurately known from the determinations of Rayleigh and Guye, were selected for experiment. For this purpose carbon dioxide and sulphur dioxide were chosen, and the results showed that the method worked satisfactorily, the variations being within the limits of accuracy aimed at.

The pressure was corrected for temperature by the simple formula $p_t = p_0(1 + 0.0001818t)$ where t is the temperature of the column of mercury. The manometer tube was 6 mm. wide, so that the correction for capillarity may be neglected. The correcting factor (0.99971) for reducing the weights from the value of gravity at Cambridge to that at Paris, may also be neglected as the difference is not within the limits of accuracy aimed at.

Carbon Dioxide.—This gas was prepared by heating together an intimate mixture of fused boric acid and recently ignited sodium carbonate, and passing the gas through a tube containing some pure phosphorus pentoxide distilled in oxygen. The apparatus for the preparation of this gas was sealed on to the inlet tube D beyond the stopcock and was thoroughly exhausted by means of a special charcoal reservoir and then finally connection was made to the previously exhausted flask A. The apparatus was allowed to stand for some time, and the special charcoal bulb sealed off. The large flask A was then ready to be filled with carbon dioxide through the inlet tube D.

The following results were obtained:—

| Pressure corrected. | Weight of gas. | Weight of 1 litre of the gas. | Vapour density of gas, taking 1 c.c. of H 0.00009 gramme. |
|---------------------|----------------|-------------------------------|---|
| mm. | gramme. | gramme. | |
| 115.4 | 0.6476 | 1.972 | 21.91 |
| 206.5 | 1.1624 | 1.978 | 21.98 |
| 206.0 | 1.1600 | 1.978 | 21.98 |

Rayleigh* gives the value 1.52909 as the weight of a litre of carbon dioxide compared to air at 0° and 760 mm., which is 1.9782 gramme per litre.

Sulphur Dioxide.—Some pure dry sulphur dioxide was liquefied in a glass bulb which, with a tube containing phosphorus pentoxide, was sealed on to D

* 'Roy. Soc. Proc.,' 1897, vol. 62, p. 206.

and the whole was then, while the sulphur dioxide was frozen in liquid air, exhausted by means of a pump followed by the use of charcoal in the manner described above. The vapour could now be changed into the previously exhausted flask A to any desired pressure.

The following results were obtained :—

| Pressure (corrected). | Weight of gas. | Weight of 1 litre of gas. | Vapour density. |
|--------------------------|-----------------------------|------------------------------|-----------------|
| mm. 76·1 198·5 | gramme. 0·6200 1·6243 | grammes. 2·863 2·875 | 31·81 31·94 |

Guye* takes 2·9266 as the most probable value for the weight of a litre of sulphur dioxide at 0° C. and 760 mm. The theoretical value of the vapour density is 31·79.

Ether.—The experiments were carried out substantially as described for sulphur dioxide.

The results obtained were as follows :—

| Pressure. | Weight of vapour. | Vapour density. |
|---------------------|-----------------------------|-----------------|
| mm. 31·4 63·9 | gramme. 0·2968 0·6024 | 36·90 36·91 |

Theoretical value of the vapour density is 36·76.

Nickel Carbonyl.—In this case a small bulb was sealed on to D, which was connected, by means of a constricted tube and a stopcock, with another bulb containing pure dry nickel carbonyl. The first bulb was exhausted with the whole apparatus, the tap at D was shut, nickel carbonyl was admitted into this small bulb, this was then cooled to -183° , the constricted tube sealed off, and the whole apparatus exhausted, while the bulb containing nickel carbonyl was kept in liquid air.

The following results were obtained :—

| Pressure. | Weight of vapour. | Vapour density. |
|-----------------------------|---------------------------------------|-------------------------|
| mm. 16·6 41·7 46·8 | gramme. 0·3600 0·9046 1·0164 | 84·67 84·69 84·79 |

* 'Compt. Rend.,' 1907, vol. 144, p. 1360.

Taking the atomic weight of nickel as 58.3 ($H = 1$).—The theoretical vapour density is 84.73, whereas on the assumption of the atomic weight suggested by Barkla and Sadler reduced to the same standard it would be 86.05. A slight deposit of nickel, due to dissociation of the nickel carbonyl under low pressure, formed on the tube just inside the tap D, where the vapour entered the apparatus. This would, of course, tend to make the result obtained too low; the amount of nickel deposited, even after several experiments, was so small, however, that its influence on the vapour density would be quite outside the limits of error. No correction was made for the presence of vapour of mercury. Taking into consideration the fact that the deviation of the vapour from the gas laws would tend to make the result too high, it is probable that the value found is not too low, and makes it impossible that the atomic weight of nickel should be as high as 61.4 relative to the oxygen standard, or 60.95 when hydrogen is taken as the fundamental unit of atomic weights.

The accuracy of the method could be greatly improved by the use of a larger vessel and more delicate manometric measurement, so that good results might be obtained at very much lower pressures. Further, if the charcoal condenser F was made of metal instead of glass, any increase of pressure on heating the charcoal up to the ordinary temperature would be immaterial, and thus more volatile gases like oxygen and nitrogen could be equally well manipulated.

(2) *Rotatory Power of Organic Substances.*

The optically rotatory power of organic substances does not appear to have been examined at temperatures below $0^{\circ}C$. An attempt to determine the change which takes place in the rotatory power of some substances down to much lower temperatures is here recorded.

With this object in view, solutions of various optically active substances in alcohol and in petroleum ether were cooled to a low temperature by means of liquid air, and it was found that solutions of a number of substances could be solidified without losing their transparency.

A jacketed polarimeter, 10 cm. in length, was made entirely of metal, and surrounded with a thick covering of wool. Experiments were made to find out how best to avoid the deposition of hoar frost on the glass plates at the ends of the tube. This caused some trouble, and, after trying a number of devices, it was found that, when the glass plates used to close the ends of the tube were about 1 cm. thick, and their outer surfaces were continually moistened with absolute alcohol, readings could be taken at quite low temperatures.

Cooling was carried out by introducing liquid air, or other liquids of low boiling-point, into the cylindrical space between the actual tube and the outer jacket. Cooling caused distortion of the field of the polarimeter as seen through the liquid, and accurate determinations of the rotatory power soon became impossible; however, by cooling slowly, and allowing a considerable time for inequalities in density to disappear, it was found that fairly consistent readings of the polarimeter could be obtained, and the uncertainty in the result was usually not greater than $0^{\circ}3$. When the liquid in the tube solidified to a transparent glass, readings were no longer possible, as the field of the polarimeter became uniform in all positions of the analyser; this effect is probably due to double refraction, caused by strain. In the case of some solutions, such as that of menthol in alcohol, this effect appeared at -80°C ., while the solution was still liquid.

The choice of solvents is practically limited to ethyl alcohol and petroleum ether of low boiling point, since these are among the few liquids which solidify below -100°C . to a transparent glass.

It soon became clear also that very few active substances were suitable for examination, as it was necessary to get a sufficiently large rotation to observe, and solutions of most substances, when concentrated enough to give a rotation as large as desirable, could not be cooled and still retain their transparency.

Solutions of a number of substances have been examined, but two only need be mentioned here as it is hoped later to communicate the results of further experiments on the effect of temperature on rotatory power.

These two substances are *l*-nicotine and "bitter orange oil," consisting chiefly of *d*-limonene. These were chosen for several reasons: first, on account of their great rotatory power, $[\alpha]_{\text{D}} = -163^{\circ}$ and $+96^{\circ}$ respectively; secondly, they both formed mixtures with alcohol which could be solidified to transparent glasses, and, thirdly, on account of the difference in their behaviour within the limits of temperature hitherto examined. The rotatory power of nicotine increases with increase of temperature, while that of limonene decreases with increase of temperature.

The following observations are selected from those made and illustrate the kind of change observed.

Nicotine.—Solution in alcohol, 21.2 grammes in 100 c.c. at 20°C . Density, 0.871.

| Temperature. | Observed rotation. |
|--------------------------|--------------------|
| + 20°C . | $-30^{\circ}0$ |
| — 50 | $-28^{\circ}7$ |
| — 70 | $-27^{\circ}3$ |
| — 90 | $-25^{\circ}3$ |
| — 120 | $-22^{\circ}0$ |

At lower temperatures readings were impossible.

Solutions of nicotine in petroleum ether on cooling soon deposit solid nicotine and are therefore useless.

It is clear from the above results that the rotatory power of nicotine diminishes with decreasing temperature below 0° C. just as it does above this temperature. Moreover, the diminution appears to be quite regular; since the curve showing the relation between the temperature and the observed rotation is approximately a straight line which, when produced, gives a rotation at the absolute zero of about 12° .

The specific rotatory power cannot be calculated, since the densities of the solution at the different temperatures have not been determined.

A rough estimate of the specific rotatory power can, however, be obtained by using the densities of alcohol calculated from a Waterston formula, $V = 2.8911 - 0.6938 \log(243.6 - t)$. The density of alcohol at -90° C. would be, according to this formula, 0.877. The density of the nicotine solution at 20° C. was 0.871, and may be assumed to be about 0.95 at -90° C., hence the specific rotatory power at this temperature would be approximately -109° .

Taking the value of the observed rotation from the curve to be $-23^{\circ}.5$ at -115° C., the density of alcohol to be 0.894, and that of the solution to be 0.97, we get the specific rotatory power at this temperature to be about -99° . Hence, by extrapolation of the linear law, the specific rotatory power at -273° C. would be about -54° .

Bitter Orange Oil.—Solution in alcohol, 20 grammes in 100 c.c. at 15° C. Density, 0.816.

| Temperature. | Observed rotation. |
|------------------|---------------------|
| + 8° C. | + $18^{\circ}.5$ C. |
| —35 | 20.5 |
| —65 | 22.3 |
| —85 | 24.5 |
| —95 | 25.5 |

Further readings were impossible.

The curve expressing the relation between temperature and observed rotation was found to be practically a straight line, and the value of the observed rotation at the absolute zero would be about 37° . The rotatory power, therefore, increases with diminishing temperature below 0° C. as it does above this temperature. On calculating the densities of the solution in the same rough way as in the case of the nicotine solution, we get the density of the solution at -90° C. to be 0.89, and hence the specific rotatory power would be about $+114^{\circ}$. By extrapolation, on the assumption of the linear

238 *Application of Low Temperatures to Chemical Problems.*

law, the value of the specific rotatory power at -273° C. is found to be about 156° .

Solution in petroleum ether (B. P. 30° — 35° C.), 20 grammes in 100 c.c. at 15° C.

| Temperature. | Observed rotation. |
|------------------|---------------------------|
| + 5° C. | + $19^{\circ} \cdot 2$ C. |
| —15 | 20 \cdot 5 |
| —35 | 22 \cdot 2 |
| —60 | 23 \cdot 7 |
| —75 | + 24 \cdot 2 |
| —95 | 26 \cdot 0 |

Further readings were impossible.

The results in this solvent are therefore just the same as those in alcohol, the rotatory power increases with diminution of temperature and would be about 40° at absolute zero, if the linear law be extended.

Similar results have been obtained with a number of other substances such as menthol, camphor, ethyl tartrate, and pinene, but on account of the smaller rotations that were observed they were not so regular nor so conclusive. It would therefore appear from these preliminary observations that the rotatory power of optically active carbon compounds in solution changes in a regular manner with temperature down to -120° C. and that the molecules would, in all probability, still exhibit optical rotatory power at much lower temperatures.



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*Address of the President, Lord Rayleigh, O.M., D.C.L., at the
Anniversary Meeting on November 30, 1907.*

Since the last Anniversary the Society has sustained the loss of twenty-five Fellows and three Foreign Members.

The deceased Fellows are :—

| | |
|-----------------------------------|-----------------------------|
| Thomas Andrews, | Rev. John Kerr, |
| Sir Benjamin Baker, | Sir Leopold McClintock, |
| Sir Dietrich Brandis, | Dr. Maxwell Tylden Masters, |
| Sir William Henry Broadbent, | Prof. Alfred Newton, |
| Dr. Alexander Buchan, | Cornelius O'Sullivan, |
| Lord Davey, | Sir William Henry Perkin, |
| Dr. August Dupré, | Dr. William Henry Ransom, |
| Sir Joseph Fayrer, | Sir Edward James Reed, |
| Sir Michael Foster, | Dr. Edward John Routh, |
| Sir William Tennant Gairdner, | Henry Chamberlaine Russell, |
| Lord Goschen, | Prof. Charles Stewart, |
| Sir James Hector, | Robert Warington. |
| Prof. Alexander Stewart Herschel, | |

The Foreign Members are :—

Marcellin Berthelot, Dmitri Ivanovitch Mendeleeff, Henri Moissan.

From the length of this list it will be seen that death has been unusually busy during the year. It includes many names of great distinction, of whom I can refer only to a few.

Sir B. Baker was a Councillor at the time of his death, and was well known among us as a frequent attendant at our meetings and as combining scientific interests with the highest degree of successful practice in his profession. The recent catastrophe in America will, perhaps, even enhance his reputation as the designer of the Forth Bridge.

In Sir Michael Foster we have lost one, to whom probably more than to anyone else the present position of our Society is due. For 22 years he held the office of Secretary, during about half of which time I was his colleague. It would not be too much to say that the interests of the Society and a desire to extend its usefulness were never out of his mind. It was inevitable that his pronounced views and his energy in giving effect to them should occasionally arouse opposition, but he was impelled always by public spirit, sometimes to the detriment of his own private interests. His work for Cambridge, for the Government in commissions of inquiry, as well as for the Society, constitute a lasting claim upon the gratitude of our generation.

The name of Kerr will go down to posterity as the discoverer of two remarkable phenomena in Electro-Optics. His success is a good example of what may be accomplished under no small difficulties by courage and perseverance.

The claims of Sir W. Perkin as the pioneer in the aniline industry and as a distinguished worker in scientific chemistry have recently been celebrated, and are recognised all over the world. It is satisfactory to reflect that, unlike many inventors, he met with full appreciation during his lifetime.

Dr. Routh's name is one that I cannot allow to pass without a word. I was indebted to him for mathematical instruction and stimulus at Cambridge, and I can still vividly recall the amazement with which, as a freshman, I observed the extent and precision of his knowledge, and of the rapidity with which he could deal with any problem presented to him. His book on Dynamics is well known. In its earlier editions it illustrated, perhaps, rather the vices than the virtues of the Cambridge School, but it developed later into a work of first-rate importance. I have always been under the impression that Routh's scientific merits were underrated. It was erroneously assumed that so much devotion to tuition could leave scope for little else.

On the foreign list we have to lament three chemists of high distinction, Berthelot and Mendeleeff, though still active, had attained old age; but in Moissan we lose one from whom much more might have been expected. All three have been recipients of our medals.

An important feature in the work of the Royal Society consists of various enquiries, undertaken for different Departments of Government, in regard to diseases which affect the tropical portions of our foreign possessions and dependencies. Among these diseases the attention of the civilised world has been for some years directed to the malady known as Sleeping Sickness. The first concerted action for the study and combating of this appalling scourge arose out of a representation made by the Royal Society to the Foreign Office in the spring of 1902, in consequence of which, at the request of the Treasury, the Society's Malaria Committee organised and despatched a small scientific commission to Uganda. In the course of a short time the source of the disease was traced by this Commission to the presence of a trypanosome in the blood and cerebro-spinal fluid of the victims, and the further discovery was also made by the same Commission that the trypanosomes are carried by a species of biting tsetse-fly. These important revelations were followed up by detailed studies of the character and distribution both of the disease and of the fly. Besides sending out a succession of observers to prosecute the investigations of its Commission at Entebbe, the Royal Society urged upon the Colonial Office the necessity of organising, and under an increased

ical staff, a more comprehensive enquiry into the local conditions under which the disease is propagated. This recommendation was carried out and a valuable information on the subject has been obtained. Meanwhile, though various drugs had been tried with at best only temporary success, no lasting remedy had been found for the malady, which has continued to be local and to spread steadily over Central and East Africa. The various European Governments which have possessions in those regions have at last agreed to make a united effort to cope with Sleeping Sickness through the instrumentality of an International Conference having a separate bureau in each country concerned and a central bureau in London. The object of this co-operation will be to collect information bearing on the disease, to conduct and carry out such scientific researches as may seem to be necessary to concert measures for dealing with the disease and the populations threatened or likely to be affected by it. The Royal Society, having led the way in this subject, has been invited to give the proposed combined international action its support. The Society welcomes the proposal and will be prepared to render every assistance in its power. In the meantime our Tropical Diseases Committee is continuously and actively engaged in the endeavour to discover a drug that may prove effective in the treatment of the disease. Their investigations have been directed to the study of trypanosomiasis in rats and the latest results obtained are such as to encourage the hope that at least in this direction their labours have been successful.

During the present year three parts of the Reports of the Society's Mediterranean Fever Commission have been published, embodying the final observations and conclusions in this important enquiry, which was undertaken at the joint request of the Admiralty, War Office, and Colonial Office. It is often that a difficult investigation of this kind can be brought to a successful conclusion in so short a time as two years and a-half, and the able members of the Commission are deserving of the warmest commendation for the skill, zeal, and promptitude with which they have solved the problem submitted to them. They have shown how the scourge of fever, which has been so long rife in Malta, and has so seriously reduced the strength of our garrison there, may be eventually banished from the island. Already their recommendations, so far as they have been followed, have reduced the amount of fever to trifling proportions. It now remains for the authorities to adopt the further precautions pointed out to them, which will probably banish the disease altogether.

have continued to preside at the Meetings of the Executive Committee of the National Physical Laboratory.

The work of the Laboratory has grown greatly during the year. The addition to the Engineering Building and the new building for Metallurgical Chemistry are completed and are now occupied, while the building for Metrology is very nearly finished.

A new 100-ton testing machine, one of Messrs. Buckton's latest patterns, has been installed, and the increased accommodation in the Engineering Laboratory enables the work there to proceed more easily and rapidly.

Great progress has been made in the equipment of the Electro-technical Laboratory, and research and test-work can now go on there in a rapid and systematic manner.

The question of the Commercial Testing undertaken by the Laboratory has been the subject of investigation by a Treasury Committee, before which I was summoned to give evidence. It is understood that the report of this Committee may be expected shortly.

Progress has been made with the buildings at Eskdale Muir, some of which are now ready for occupation. It was hoped that the work might have begun this summer, and the Treasury have provided a sum of £750 for the expenses during three-quarters of the current financial year. Owing to the bad weather in the early summer this anticipation has not been realised, but a start will be made very shortly. The buildings are admirably adapted for their purpose, and will render possible the study of terrestrial magnetism under the undisturbed conditions which used to exist at Kew.

A list of the more important researches is published in the Report of the Laboratory. Among these may be mentioned those by Dr. Harker on the Kew Scale of Temperature and its relation to the International Hydrogen Scale; Mr. Paterson's paper, read before the Institution of Electrical Engineers—"Investigations of Flame Standards and the Present Performance of High-voltage Lamps"; and the eighth report of the Alloys Research Committee, by Dr. Carpenter and Mr. Edwards, on the Properties of Alloys of Aluminium and Copper. Professor Ayrton, Mr. Mather, and Mr. Smith have finished their work on the Ampere Balance, and the paper is now being published in the 'Philosophical Transactions,' while papers on the Silver Voltameter and the Weston Cell are also in the press.

Dr. Stanton and Mr. Bairstow have completed a further research on the measurement of wind pressure, and are well advanced with the investigation into methods of impact-testing.

Other researches in progress are those on the measurement of small inductances and capacities, with a view to the standardisation of the wavelengths used in wireless telegraphy, on alloys of copper, aluminium, and manganese, for the Alloys Research Committee, and on the properties of eutectics.

The completion of the work on the electrical units will be satisfactory to those who have been interested in this question. At the time of my own researches about twenty-five years ago, the ohm and the ampere were uncertain to 2 or 3 per cent., and I then scarcely hoped to get nearer than one part in a thousand. The recent work carried on at Bushey would seem to indicate that an accuracy of one part in ten thousand may have been attained. The possibility of such a refinement depends largely upon the use in the instruments of coils composed of a single layer of wire, the position of every turn of which is open to exact determination. The importance of this feature was insisted upon by the late Professor Jones.

Accuracy of measurement appeals less to the lay and scientific public than discoveries promising to open up new fields; but though its importance at any particular stage may be overrated, it promotes a much needed consolidation and security in the scientific edifice. A remarkable example of enhanced accuracy is afforded by modern measurements of luminous wave-lengths, for which we are mainly indebted to our Copley medallist. Not only did he introduce the vacuum tube charged with mercury or cadmium as the best source of homogeneous light, but by a most able use of an ingenious method he determined, with the highest precision, the values of the cadmium red, green, and blue wave-lengths in terms of one another, and of the metre. His work has been skilfully followed up by Fabry and Perot, and numerous wave-lengths are now known with a relative accuracy of one-millionth part. When we reflect upon the almost ultra microscopic magnitude of a wave-length of light, the possibility of such an achievement may well excite our astonishment.

For the advancement of science the main requirement is, of course, original work of a high standard, adequately explained and published. But this is not enough. The advances so made must be secured, and this can hardly be, unless they are appreciated by the scientific public. In some branches of Pure Mathematics it is said that readers are scarcer than writers. At any rate the history of science shows that important original work is liable to be overlooked and is perhaps the more liable the higher the degree of originality. The names of T. Young, Mayer, Carnot, Waterston, and B. Stewart, will suggest themselves to the physicist; and in other branches, doubtless, similar lists might be made of workers whose labours remained neglected for a shorter or a longer time. In looking into the more recent progress of Geometrical Optics, I have been astonished to find how little correlation there has been between the more important writings. That Coddington should have remained unknown in Germany and von Seidel in England need not greatly surprise us; but in this subject it would appear that a man cannot succeed in

making even his own countrymen attend to him. Coddington seems to have heard nothing of Cotes and Smith, and Hamilton nothing of Airy and Coddington.

It is true that no two writers on theoretical subjects could differ more in taste and style than do Hamilton and Coddington. The latter addressed himself to special problems, the solution of which seemed to have practical importance. Among his achievements was the rule relating to the curvature of images, generally known as Petzval's, although Petzval's work was of much later date. Hamilton, on the other hand, allowed his love of generality and of analytical developments to run away with him. In his *Memoir on Systems of Rays*, with its elaborate and rambling supplements, there is little to interest the practical optician, though the mark of genius is throughout apparent. It was only in two or three pages of a later paper that he applied his powerful methods to the real problem of Optics. As Finsterwalder has remarked, his "six radical constants of aberration," expressing the general properties of a symmetrical instrument, are at once an anticipation and a generalisation of von Seidel's theorems. But the published work is the barest possible summary. If Hamilton had been endowed with any instinct for Optics proper, he could have developed these results into a treatise of first-class importance. In more recent times Hamilton's footsteps have been followed by Maxwell as well as by Thiesen and Bruns, of whom the two latter do not seem to have realised that Hamilton (or even Maxwell) had concerned himself with the subject at all. The natural development of Hamilton's ideas will be found in an able memoir by Schwarzschild (1905).

I have spoken of English work that lay neglected, but a scarcely less notable instance is the splendid discovery of the microscopic limit by Fraunhofer, a man who combined in the highest degree practical skill with scientific insight. Thanks to the researches of Abbe and Helmholtz, it is now well known that there is a world that lies for ever hidden from our vision, however optically aided; but neither of these eminent men realised that the discovery had been anticipated by Fraunhofer. Some, perhaps, may doubt whether Fraunhofer's argument, founded upon the disappearance of spectra from gratings of extreme fineness, is of adequate cogency. To this I may reply that I was myself convinced by it in 1870, before either Abbe or Helmholtz had written a word upon the subject.

Enough has probably been said to illustrate my contention that much loss has ensued from ignorance and neglect of work already done. But is there any remedy? I think there ought to be. In all the principal countries of the world we have now a body of men professionally connected with science in its various departments. No doubt the attention of many of these is so

engrossed by teaching that it would be hard to expect much more from them, though we must remember that teaching itself takes on a new life when touched with the spirit of original enquiry. But in the older Universities, at any rate, the advancement of science is one of the first duties of Professors. Actual additions to knowledge occupy here the first place. But there must be many who, from advancing years or for other reasons, find themselves unable to do much more work of this kind. It is these I would exhort that they may fulfil their function in another way. If each man would mark out for himself a field—it need not be more than a small one—and make it his business to be thoroughly conversant with all things new and old that fall within it, the danger of which I have spoken would be largely obviated. A short paper, a letter to a scientific newspaper, or even conversation with friends and pupils, would rescue from oblivion writings that had been temporarily overlooked, thereby advancing knowledge generally and sometimes saving from discouragement an unknown worker capable of further achievements. Another service such experts might render would be to furnish advice to younger men desirous of pursuing their special subject.

The readers of whom I have been speaking are experts capable of advancing science themselves and of helping others to do so. But there is another class of possible readers of scientific books on behalf of whom I wish to make an appeal. We who are dependent upon sight in almost everything that we do must specially sympathise with those unfortunates who are deprived of this most precious gift. A movement is on foot, and has already received valuable support, to promote the publication of standard scientific works in embossed type suitable for the use of the blind. Such publication is costly and can hardly be undertaken upon an adequate scale without external aid. My friend, Mr. H. M. Taylor, a Fellow of this Society, tells me that in the course of the last 12 months he has written out the whole of Mr. C. Smith's Elementary Algebra in Braille type, has afterwards read the copy with his fingers and again, later, read the whole in proof. There can be no doubt that books in embossed type on such subjects as Mechanics, Physics, Astronomy, Geology, not to mention the various Biological Sciences, would be an immense boon to many blind readers. I commend the proposal heartily to your notice.

Another remedy for the confusion into which scientific literature is liable to fall may lie in the direction of restricting the amount of unessential detail that is sometimes prevalent in the publication of scientific results. In comparing the outputs of the present time, and of, say, 30 years ago, the most striking feature that appears is doubtless the increase of bulk, in recent

years coming especially from young workers stimulated by the healthy encouragement of direct research as a part of scientific education. But I think it may also be observed, and not alone in the case of such early dissertations, that there is, on the whole, less care taken for the concise presentation of results, and that the main principles are often submerged under a flood of experimental detail. When the author himself has not taken the trouble to digest his material or to prepare it properly for the press, the reader may be tempted to judge of the care taken in the work from the pains taken in its presentation. The tendency in some subjects to submit for immediate publication the undigested contents of note-books is one that we hear much of at the present time. It is a matter that is difficult for publishing bodies to deal with, except by simple refusal of imperfectly prepared material, with its danger of giving offence to authors of recognised standing, but it seems not unlikely that at present public scientific opinion would endorse such a course of action. A related difficulty and one that contributes to this trouble, is the tendency, noticeable in some public scientific organisations, to imagine that their activity is estimated by the number of pages of printed matter they can produce in the year. Probably no consideration is further removed than this from the minds of the educated public, whose judgment is alone worth considering.

MEDALLISTS, 1907.

COPLEY MEDAL.

The Copley Medal is awarded to Professor Albert Abraham Michelson, For. Mem. R.S., on the ground of his experimental investigations in Optics.

In 1879, Michelson brought out a determination of the velocity of light by an improved method, based on Foucault's, which gave 299,980 kilometres per second. Three years later, by means of a modification of the method, capable of even greater precision, he found for this constant, of fundamental importance for electric as well as optical science, the value of 299,853 kilometres.

Michelson has been a pioneer in the construction of interferometers, which are now indispensable in Optics and Metrology. With his new instrument, at Paris, he determined the absolute wave-lengths of the red, green, and blue lines of cadmium by counting the number of fringes (twice the number of wave-lengths) corresponding to the length of the standard metre of the Bureau International des Poids et Mesures. He found the metre to be 1,553,164 times the wave-length of the red line of cadmium, a result

which is almost in exact agreement with the redetermination last year by Perot and Fabry. Michelson thus proved the feasibility of an absolute standard of length, in wave-lengths, of such accuracy, that if the standard metre were lost or destroyed, it could be replaced by duplicates indistinguishable from the original.

He had the greatest share in the elaboration of precise experiments on the relative motion of ether and matter. He repeated in an improved form Fresnel's experiment of the speed of light in moving media, using water and sulphide of carbon. He found that the fraction of the velocity of the water by which the velocity of light is increased is 0.434, with a possible error of ± 0.02 . The fact that the speed is less in water than in air shows experimentally that the corpuscular theory is erroneous; but his results, moreover, established the correctness of Fresnel's formula for the effect, the theory of which has since become well understood.

In conjunction with E. W. Morley, he devised and carried out a very remarkable method by which, on the assumption of ether at rest, an effect depending on quantities of the order $(v/V)^2$ would appear to be appreciable. No displacement of the fringes was found. Of this result the simplest explanation would be that the ether near the earth partakes fully in its orbital motion; but modern electric and optical science appears to demand a quiescent ether, and the existence of this and similar null results is fundamental for its theory.

He has shown the possible application of the Interferometer method to Astronomy, by himself measuring the diameters of the four satellites of Jupiter, which are only about one second of arc. He suggests the further application of the instrument to such of the fixed stars as may not subtend less than one-hundredth of a second of arc.

In 1898, Michelson constructed a spectroscope which enables us to make use of the great resolving powers of the very high orders of spectra which are absent in the use of the ordinary grating, and with the added advantage of having most of the light in one spectrum. The echelon consists of a pile of glass plates of precisely equal thickness, which overlap by an equal amount; with it spectral lines which appear single with the most powerful gratings can be resolved into components. This instrument has been especially useful for the direct observation of the important, because definite, influence of magnetism on light, discovered by Zeeman. With 30 plates, and using the 25,000th spectrum, the echelon has a resolving power of 750,000, while the most powerful gratings do not exceed 100,000.

In connection with the analysis of radiations, he has constructed and used various machines for the analysis of periodic motions. For example, in

conjunction with Stratton, he perfected a remarkable machine which is based on the equilibrium of a rigid body under the action of springs.

Professor Michelson has also investigated by his Interferometer the important subject, both theoretically and practically, of the breadth and the structure of spectral lines, including the effect of a magnetic field, and in various other ways his genius has opened up new ground in experimental Optics.

ROYAL MEDALS.

One of the Royal Medals has been awarded, with the approval of His Majesty, to Dr. Ernest William Hobson, F.R.S.

During the last 20 years Dr. E. W. Hobson has been distinguished for the fundamental character of his contributions to Mathematics and Mathematical Physics. His earlier published work, from 1888 onwards, deals largely with the so-called Harmonic Analysis, which embraces many topics having for their common aim the solution of the Potential Equation in forms suitable for application to the problems of Physics. The exhaustive examination of the general types of Harmonic Functions contained in his paper in the 'Phil. Trans.,' 1896, has been found to be of high utility for this application. He was led by these researches, and particularly by the difficulty of describing in general terms the characteristics of a function capable of being represented by Fourier's series, to take part in the revision of the logical basis of Differential and Integral Calculus which is now in progress; his Presidential Address to the London Mathematical Society, in 1902, on the questions here arising, aroused general interest among mathematicians; and he has recently (1907) published an extensive volume, dealing with the whole matter and its applications to the theory of Fourier's series, which is of great importance for the history and development of Mathematics.

His Majesty has also approved the award of a Royal Medal to Dr. Ramsay H. Traquair, F.R.S.

Dr. Traquair is honoured on the ground of his long continued researches on the fossil fishes of Palæozoic strata, which have culminated, within the past 10 years, in his discovery of new groups of Silurian and Devonian fishes, and in his complete exposition of the structure of *Drepanaspis*, *Phlyctenaspis*, and other remarkable forms.

For nearly forty years Dr. Traquair has been busy with the description of fossil fishes, mostly from the Palæozoic rocks of Scotland, and he is deservedly held to be one of the most eminent palæontologists of the day. He has been highly successful in the interpretation of the often very obscure and frag-

mentary remains which he has had to elucidate, and his restorations of fishes have won such credit as to appear in all modern text-books of Palæontology. It may be said that his work, notwithstanding the great difficulties of the subject, has well stood the test of time.

Dr. Traquair has done much to advance our knowledge of the osteology of fishes generally. His earliest memoirs on the asymmetrical skull of flat-fishes and on the skull of *Polypterus* remain models of exactness. His acquaintance with osteology enabled him to show how former superficial examination of the Palæozoic fishes had led to wrong interpretations. He demonstrated that *Chirolepis* was not an Acanthodian, as previously supposed, but a true Palæoniscid. In 1877 he satisfactorily defined the Palæoniscidæ and their genera for the first time, and conclusively proved them to be more nearly related to the Sturgeons than to any of the other modern Ganoids with which they had been associated. He thus made an entirely new departure in the interpretation of extinct fishes, replacing an artificial classification by one based on phylogenetic relationship. His later memoir on the Platysomidæ was equally fundamental and of the same nature.

All subsequent discoveries, many made by Traquair himself, have confirmed these conclusions, which are now universally accepted.

In 1878, Dr. Traquair demonstrated the Dipneustan nature of the Devonian *Dipterus*, and somewhat later he began the detailed study of the Devonian fishes. His latest researches on the Upper Silurian fishes of Scotland are equally important, and provide a mass of new knowledge for which we are indebted to his exceptional skill and judgment in unravelling the mysteries of early Vertebrate life.

DAVY MEDAL.

The Davy Medal is awarded to Professor Edward Williams Morley.

Professor Edward W. Morley is well known both to chemists and to physicists for his work in the application of optical interferences and other physical phenomena to increase the accuracy of measurement. Numerous valuable papers have appeared, either in collaboration with Professor Michelson and others, or in his own name, on such subjects. Special reference may be made to his experiments, in conjunction with Professor Michelson, on the fundamental question of the absence of effect of translatory motion of material bodies on luminous phenomena.

His claim to the Davy Medal rests on grounds closely related to these researches; for he has combined thorough mastery of accurate measurement with an intimate knowledge of modern chemistry, and has utilised them in his attempt to solve one of the most difficult and fundamental problems of

chemical science. The special problem to which he has consecrated many years of his life is the determination of the relative atomic weights of hydrogen and oxygen; it has been attacked by him with rare insight and skill, and with indomitable perseverance, and he seems to have settled it for many years to come, if not permanently. All the recent work devoted to this problem, and there has been much, has tended to establish more firmly the ratio arrived at by Professor Morley.

His determinations of the absolute weights of a litre of hydrogen and of oxygen, and his investigations of the amounts of moisture retained by gases dried by various desiccating agents, are of the very greatest importance for scientific progress.

SYLVESTER MEDAL.

Professor Wilhelm Wirtinger, of Vienna, is the recipient of the Sylvester Medal.

He is distinguished for the importance and wide scope of his contributions to the general Theory of Functions. Our knowledge of the general properties and characteristics of functions of any number of independent variables, and our ideas for the further investigation of such functions are, for the most part, at present bound up with the Theory of Multiply-periodic Functions, and this Theory is of as great importance for general Solid Geometry as the ideas of Abel have proved to be for the Theory of Plane Curves. Professor Wirtinger has applied himself for many years to the study of the general problems here involved. A general summary of his researches is given by him in the Abel Centenary volume (xxvi, 1902) of the 'Acta Mathematica.' Two of his papers may be particularly referred to, both of 1895. One of these deals with the reduction of the Theory of General Multiply-periodic Functions to the Theory of Algebraic Functions, with a view to their expression by Theta functions; this was one of the life problems of Weierstrass, who did not, however, during his lifetime, publish anything more than several brief indications of a method of solution. Professor Wirtinger's memoir obtains a solution, and is, moreover, characterised throughout by most stimulating depth and grasp of general principles. This paper was followed by two others, one continuing the matter in detail, the other making an application of its principles to the general Theory of Automorphic Functions. Another extensive paper, which obtained the Beneke Prize of the Royal Society of Göttingen, deals with the general Theory of Theta Functions. In it he obtained results of far-reaching importance, for Geometry as well as for the Theory of Functions, the full development of which will require many years of work.

HUGHES MEDAL.

The Hughes Medal is awarded to Principal Ernest Howard Griffiths. Principal Griffiths has conferred great benefit on physical science by his series of measurements of fundamental constants, mainly in the domain of thermal and electric energy. At a time when the equivalent of the thermal unit in mechanical energy stood urgently in need of revision, he devoted himself to the problem with all the refinements and patient manipulation that could be devised, the result being a value for Joule's equivalent which has since once acquired authority in the light of the evidence produced, and has fully confirmed the corrections already advanced by Rowland and others. The main cause of discrepancy had been found to be the variation of the thermal capacity of water with the temperature; and by an investigation in which this variation was determined, Griffiths elucidated and correlated fundamentally the work of previous observers, from Joule onward. Of special importance also, in the domain of chemical physics, was an investigation of the depression of the freezing point of water by very dilute mixture of dissolved substances, wherein he verified, with all the refinement of absolute physical determinations, that the change of freezing point ran exactly parallel to the electric conductivity when the dilution of electrolysable salt was comparable to that of gases, being twice as much per molecule as the standard value of the depression for non-electrolytes.

BUCHANAN MEDAL.

The Buchanan Medal is awarded to Mr. William Henry Power, C.B., F.R.S. Mr. Power's services to Hygienic Science and Practice have extended over a period of more than thirty years, and have been of the most distinguished kind. He has himself personally conducted successful enquiries into the causes of the spread of various diseases, and has obtained results which have proved of the greatest benefit to mankind. Moreover, in his long connection with the medical department of the Local Government Board, he has planned and directed numerous general and local investigations whereby our knowledge of disease, and of the methods of coping with it, have been greatly increased. The medical reports issued by the Local Government Board, which are universally regarded as among the most important contributions of our time to this subject, have for many years past been either written by him or owe much to his editorial criticism and supervision. It is not too much to say that no living man in this country has advanced the cause of scientific hygiene more than Mr. Power, or is more worthy of the distinction of the Buchanan Medal.

*On the Non-Periodic or Residual Motion of Water
Moving in Stationary Waves.*

By MRS. HERTHA AYRTON.

(Communicated by Professor J. H. Poynting, F.R.S. Received December 7, 1907,
—Read January 30, 1908.)

[PLATES 4—6.]

It is well known that when water moves in stationary waves, the particles do not, like pendulums, simply swing to and fro, returning after each oscillation to the points from which they started; but that each element takes up a new position after each oscillation, so that it traces out a path for itself, only returning after many oscillations to its starting point. Part of this non-periodic or residual motion, as I shall call it, in stationary waves, has been traced out mathematically by Lord Rayleigh. The object of the present paper is to show, experimentally, what it is, as completely as possible.

In his classic paper "On the Circulation of Air observed in Kundt's Tubes, and on some Allied Acoustical Problems," Lord Rayleigh examined, among other things, the influence of the bottom of a horizontal vessel on the motion of water moving in it in stationary waves, and he came to the following conclusion: calling places of maximum horizontal motion loops, and places of maximum vertical motion nodes, "near the bottom the fluid rises from the bottom over the nodes, and falls back again over the loops, the horizontal motion near the bottom being thus directed towards the nodes and from the loops." Quite close to the bottom, on the contrary, he found that the motion was in the opposite direction, from the nodes and towards the loops. Fig 1 shows these two sets of vortices diagrammatically.

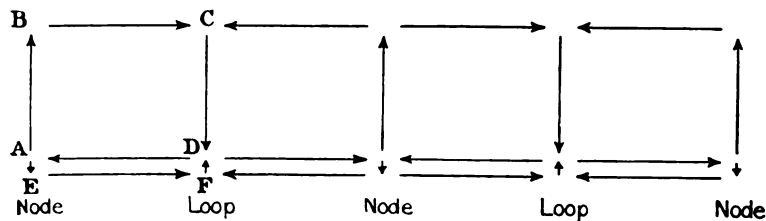


FIG. 1.—Diagram of Lord Rayleigh's Residual Vortices in one complete stationary wave of water.

In the course of some experiments on the motion of heavy particles under stationary waves, finding that it was necessary to trace out the complete

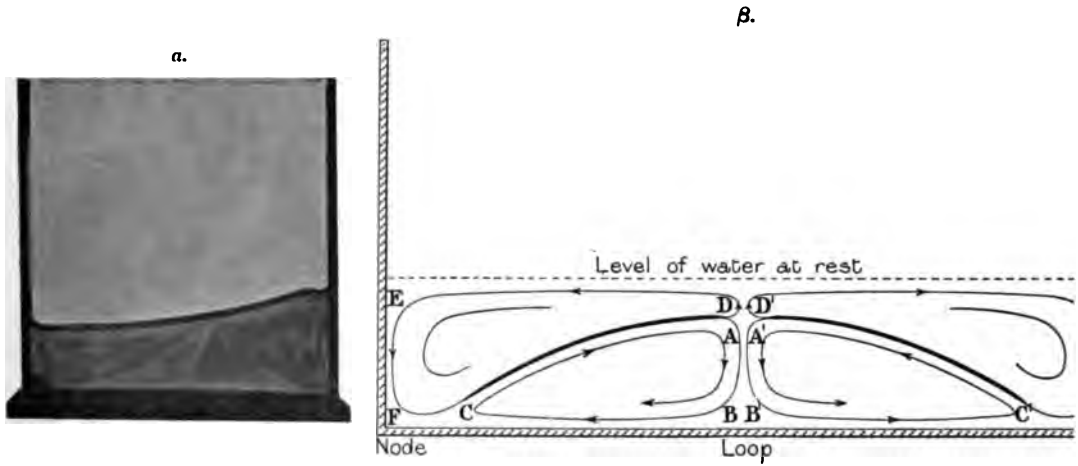


FIG. 3.

- a. Instantaneous Photograph of Water permeated with Bronze Powder, oscillating in half a stationary wave.
 b. Diagram of Residual Motion indicated by Bronze Powder in Water, oscillating in half a stationary wave. ABC, A'B'C', Lord Rayleigh's upper vortices; DEF, D'E'F', "end vortices."

(Shallow water.)

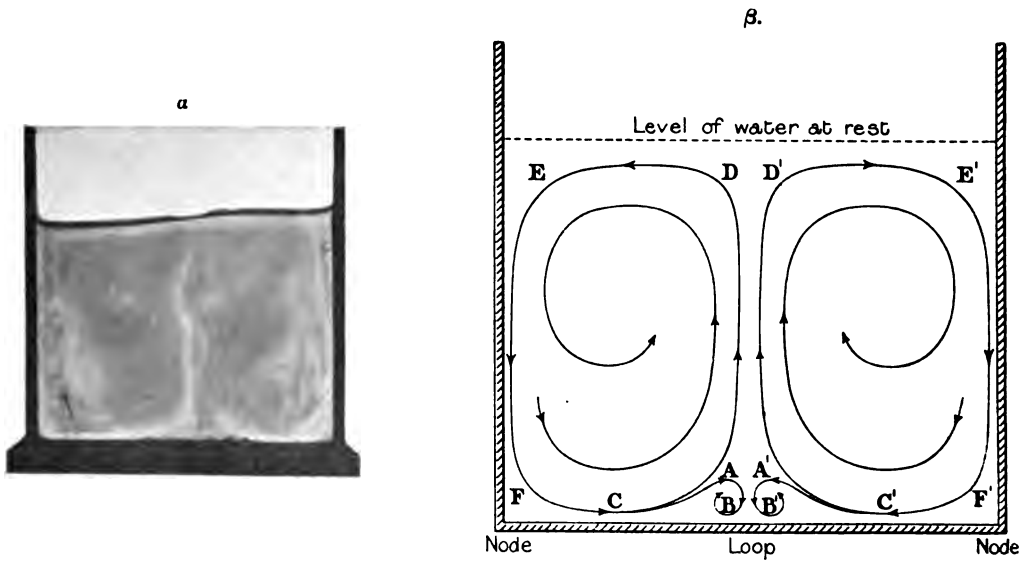


FIG. 4.

- a. Instantaneous Photograph of Water permeated with Bronze Powder, oscillating in half a stationary wave.
 b. Diagram of Residual Motion indicated by Bronze Powder in Water, oscillating in half a stationary wave. ABC, A'B'C', Lord Rayleigh's upper vortices; DEF, D'E'F', "end vortices." Depth of water nearly a wave-length.

residual motion of the water, I tried to render this visible, oscillating the water in the simplest possible way, *i.e.*, in time with its natural swing, so that it formed half a stationary wave. The first attempts, which were made in a trough 3 feet long, were entirely unsuccessful: I found it impossible, with the help of any visualising agent I could think of, to disentangle, with the eye, the residual motion from the to-and-fro movement. In a trough only 10 cm. long, however, oscillated in the same way, the residual motion to within less than a millimetre of the bottom could easily be seen, even when pepper was the visualising agent; but still better when this was replaced with bronze powder, rubbed down in a little gum with a stiff brush and then well washed.

As a certain amount of residual motion continues for some time after the oscillations have ceased, a good way to observe it is to oscillate the trough till plenty of bronze powder has been set in motion, and then to bring it to rest. When this was done with the little 10-cm. trough, Lord Rayleigh's upper vortices, ABCD, etc. (fig. 1) were clearly discernible (inner vortices, fig. 2, Plate 5) though the motion of the thin layer quite close to the bottom could not be detected in this particular way. What was plain, however, was that there was some residual motion, even quite near to the bottom, that could not be accounted for by either of Lord Rayleigh's two sets of vortices; for instead of his upper pair spreading horizontally along the whole length of the trough, as they should have done, they occupied a part of the length only—at the middle—and were flanked on either side by much more active vortices, that monopolised the whole of the ends of the trough from top to bottom. Moreover, the horizontal space occupied by each of the two sets of vortices varied with the depth of the water. When this was small compared with its length—say 1 cm. deep to 10 cm. long—Lord Rayleigh's upper vortices (ABC, A'B'C', β , fig. 3), took up most of the length of the trough, and the end vortices (DEF, D'E'F', β , fig. 3) occupied very little room at the bottom, although they always met in the middle near the top of the water. As the water was deepened, however, the end vortices became longer and the middle ones shorter (fig. 4, Plate 4) till, with water as deep as half a wave-length, the middle vortices were practically squeezed out of existence by the expanded "end vortices" (fig. 5), while small corner vortices with a languid movement appeared at F and F' (fig. 5). For these experiments with deep water I found aluminium powder better than bronze powder, on account of its lightness.

This visual test, therefore, brings out one very important point, namely, that the complete residual motion of the water, even quite close to the bottom, is dependent on the depth of the water compared with the length of

the stationary wave, and cannot be determined without taking that relation into account.

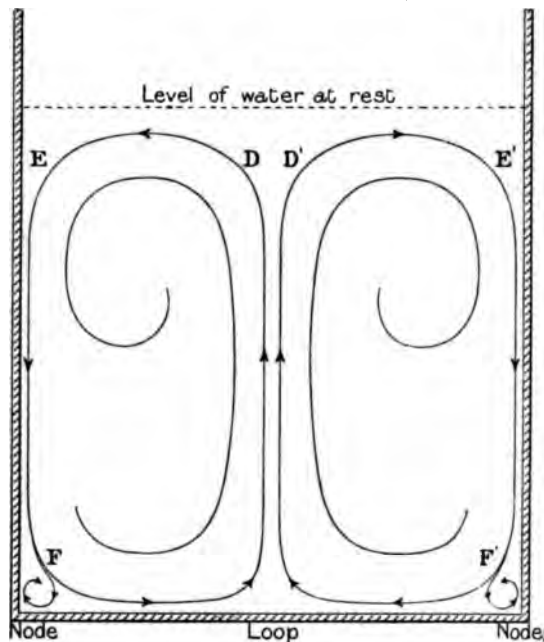


FIG. 5.—Diagram of Residual Motion indicated by Bronze Powder in half a stationary wave. Depth of water greater than half a wave-length.

The foregoing experiments were, as I have mentioned, made with water moving in half a stationary wave, so that the loop was at the middle of the trough, and the two nodes were at the ends. It now seemed important to find out whether the "end vortices" would come into play at *any* node, or whether they only appeared at nodes at the ends of the vessel. Accordingly I oscillated the water—still permeated with bronze powder—in such a way as to obtain three loops and four nodes, *i.e.*, in one and a half stationary waves. Immediately double "end vortices" came into play at each of the two interior nodes, as well as the single ones at the end nodes, so that the residual vortices appeared as shown diagrammatically in fig. 6.

Thus, what I have called "end vortices" are not confined to the ends of the trough; they come into play at each node of any series of stationary waves.

The almost vertical light line down the middle of the trough in α (fig. 4) is a good example of what is seen in all experiments with stationary waves in water permeated with visualising powder. At each vertical plane of

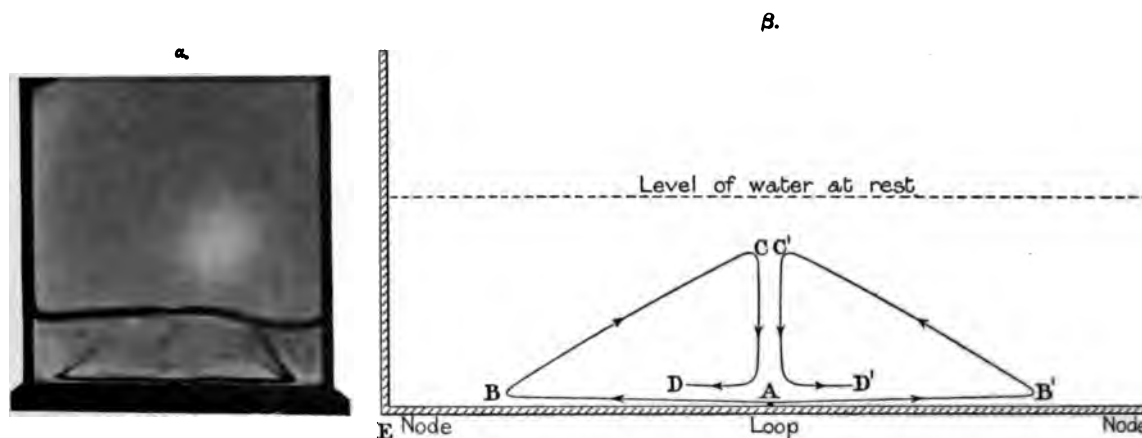


FIG. 7.

a. Instantaneous Photograph of Curves formed during first few Oscillations in Water moving in half a stationary wave, by water-colour stain placed along bottom of trough. **β.** Diagram of Curves showing Residual Motion in Water moving in half a stationary wave during first few oscillations.

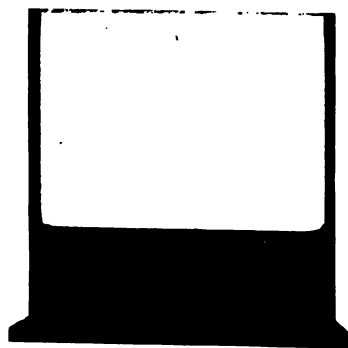


FIG. 2.—Instantaneous Photograph of Water permeated with Bronze Powder, just after it has ceased oscillating in half a stationary wave.



FIG. 8.—Instantaneous Photograph of Curves formed, during first few Oscillations in Water moving in half a stationary wave, by water-colour stain placed near middle of bottom of trough on one side.

demarcation between two residual vortices such a line is visible. These planes occur, as is clear from fig. 6, at all the loops and at all the nodes,

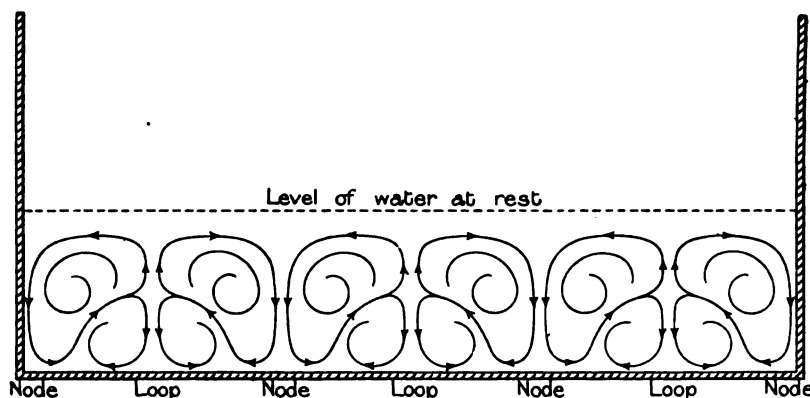


FIG. 6.—Diagram of Residual Vortices indicated by Bronze Powder in Water oscillating in one and a half stationary waves.

except the end ones, of any system of stationary waves. In α (fig. 4) where water oscillating in half a stationary wave is depicted, there is one single vertical plane of demarcation only, viz., at the loop, which is at the middle of the trough, hence the vertical line in the middle.

I have said that the visualising powder only enables one to follow the residual motion of the water to within a millimetre or so of the bottom of the trough. That means that Lord Rayleigh's thin vortices (DAEF, etc., fig. 1) cannot be detected by means of it. I noticed, however, that when the water was quite clear and only a thin layer of powder, or a small drop of water stained with water-colour paint, rested at the bottom, this rose, during the first few oscillations, in the shape shown in fig. 7, moving in the directions indicated by the arrows in the diagram (β , fig. 7). Here ABCD and A'B'C'D' were clearly Lord Rayleigh's upper vortices, and what went on close to the bottom could be inferred from the fact that a clear space of water devoid of powder quickly formed between AB, for instance, and the bottom, while the powder continued to be carried along AB and thence upwards to C and down again to D. The inference was that the powder at the bottom was being driven, by the residual current there, in the direction from E to A, so that it all gradually got carried away from the bottom back along AB, up BC, and so on. If this were so, then I had ocular proof of a part of Lord Rayleigh's thin vortices (DAEF, etc., fig. 1) between AB and the bottom (β , fig. 7); for the powder and, therefore, the residual current, went from the nodes E, E', towards the loop A along the bottom, and from the loop towards the nodes along AB, AB'.

To make sure that this inference was correct, I used clear water without powder, and squirted on to the bottom of the trough, with a pen-filler, a bright green solution near the left end, and a bright yellow one near the middle on the same side, holding the filler quite close to the bottom, so that the water should not be stained higher up. Having waited till the water had come to rest again, I then oscillated the trough as before, the idea being that the green colour would visibly travel along the bottom to the middle, while the yellow would move above it along AB and then up round CD (β , fig. 7).

This actually happened. After a few oscillations the green stain was entirely in the middle of the trough at the bottom, while the yellow travelled towards the end of the trough and then rose, as shown in fig. 8 (Plate 5), leaving a clear space at the bottom between itself and the trough; indeed, for an instant it was possible to see green travelling along the bottom towards the middle of the trough, and yellow along AB, above it, towards the end, the two colours passing one another, travelling in opposite directions; after the green had reached the centre of the trough, it also moved back to the end, and the two colours became mixed. But the first effect was very striking, and proved beyond doubt, experimentally, the existence of the residual currents along the bottom from node to loop and return currents a little higher up, from the loop towards a node, that Lord Rayleigh had predicted.

The question now arose, where does the downward flow in these thin vortices take place? There is, of course, a downward flow at the nodes, but that current extends from top to bottom of the water and belongs to the "end vortices." If Lord Rayleigh's thin vortices were separate and distinct from the "end vortices," there ought to be a downward flow at some such point as B (β , fig. 7). But the fact that the water under B always became clear so quickly after the oscillations were started, and thenceforward remained so, seemed to show that there could be no residual downward flow there, otherwise some of the stain or powder would be seen to move downwards from B to the bottom. This never happened, however; on the contrary, stain squirted right over B, even though it was, as usual, heavier than water, always travelled *upwards* along such a line as BC, but never downwards. It seemed to me, therefore, that the "end vortices" and Lord Rayleigh's thin vortices must really form one vortex of the peculiar shape shown in ABCDEFA, AB'C'D'E'F'A (β , fig. 9, Plate 6).

To test this, I squirted a little green stain on to the bottom of the trough, quite at each end, and waited till it had fallen perfectly flat. I then oscillated the trough so that the water moved in half a stationary wave, and saw the stain spread itself as shown in α (fig. 9). It first crept along the bottom to

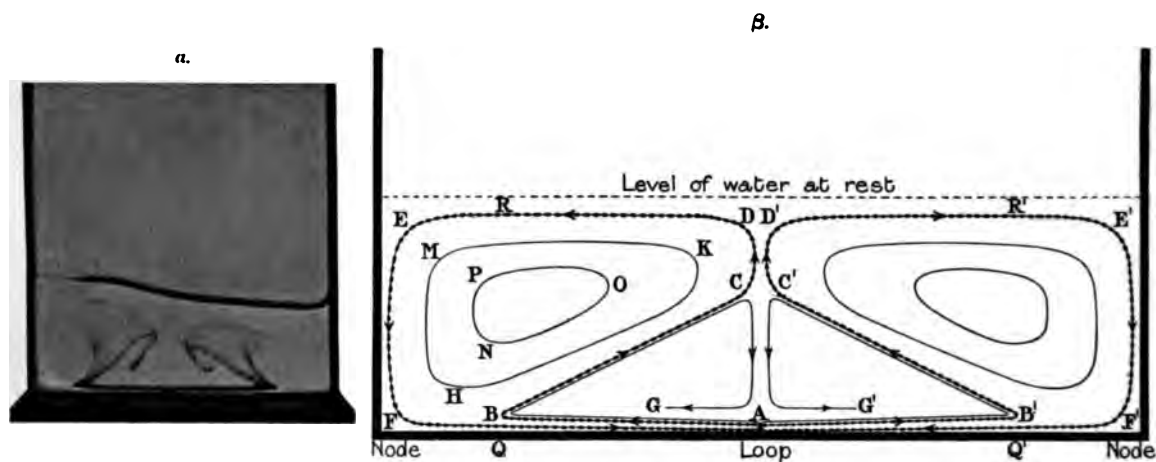


FIG. 9.

1. Instantaneous Photograph after many Oscillations of Water moving in half a stationary wave. Residual motion shown by water-colour stain placed on bottom of trough when water was at rest. β . Diagram of whole of principal Residual Vortices in Water oscillating in half a stationary wave. ABCDEFA, AB'C'D'E'F'A', outer vortices; ABCG, AB'C'G', inner vortices. Depth of water less than a quarter of a wave-length.



FIG. 10.—Instantaneous Photograph of Water moving in half a stationary wave. Residual motion shown by water-colour stain placed on bottom of trough when water was at rest. Depth of water more than a quarter of a wave-length.



FIG. 11.—Instantaneous Photograph of Water permeated with Bronze Powder, oscillating in half a stationary wave, after about six oscillations.

the middle, A (β , fig. 9) then rose up and travelled backwards in such a line as AB (taking the left side only) (β , fig. 9), then turn back again along BC, branching off at C, where part of it rose up CD and turned back along DE and down towards F, while part went down towards A and turned back towards G.

The only interpretation that it seems possible to give to such a series of motions as this is that Lord Rayleigh's thin residual vortices and the "end vortices" form part and parcel of one another and together make a vortex having an outer layer shaped like ABCDEFA (β , fig. 9). Another layer of this odd vortex must have a shape like HKM, another like NOP, and so on.

It seemed, at first, impossible to believe in the existence of even a *residual* vortex of such a form, but I have applied many tests, and each one has only shown more forcibly that this, and no other, is the real form of the vortex. I have, for instance, injected tiny drops of stain into the water at such points as N, B, H (β , fig. 9), and oscillated the water in half a stationary wave before they had had time to fall, and whichever point they were placed at they always moved as if they were being carried along by such a vortex as ABCDEFA. I have placed drops of stain successively at various points along the same horizontal line a short distance from the bottom, and watched, while oscillating in the same way, to see whether there was any sign of a downward current anywhere except at an end of the vessel—but there was none. There is, therefore, I consider, no room to doubt that, when the depth of water is less than half the wave-length, the residual motion does actually take the courses indicated in β , fig. 9.

As the pair of vortices ABCDEFA, AB'C'D'E'F'A (β , fig. 9) entirely embrace the pair ABCG, AB'C'G', I propose to call the first pair the outer residual vortices, and the second the inner ones.

In order to trace with more accuracy the exact way in which the height and length of the residual vortices altered as the water was deepened, and also to see what happened when the depth of the water was greater than half the length of the stationary wave, I used a trough 15 cm. high, 1 cm. wide, and 10 cm. long, with water-colour stain placed at the bottom while the water was still. Oscillating this so that the water formed the usual half stationary wave, I found that the inner vortices, which occupied practically the whole length of the trough when the water was very shallow, *e.g.*, 5 mm. or so deep, diminished continually in *length* as the depth of the water increased, till they disappeared when this was half a wave-length. Their *height*, on the other hand, increased at first as the water was deepened, and attained a maximum when the depth of water was about one-eighth of a wave-length. After this, the height of the inner vortices diminished again,

and became practically zero when their length became zero, *i.e.*, when the water depth was equal to half a wave-length.

As for the outer vortices, they evidently consist of three parts (β , fig. 9), REFQ occupying the whole depth of the water between a node and the nearest point to that node of the corresponding inner vortex ABCG; BC DR extending over the inner vortex to the top of the water; QAB lying between the inner vortex and the bottom. Deepening the water increases the length of REFQ and the height of BC DR, but diminishes the *length* of both BC DR and QAB, till, when the depth of the water is half a wave-length, REFQ extends the whole way from loop to node and from top to bottom of the water, except for the small place occupied by the ineffective little corner vortices already noticed, F, F' (fig. 5).

A comparison of α (fig. 7), α (fig. 9), and fig. 10 is very instructive in showing the way in which deepening the water, while retaining the same wave-length, alters the length and height of the inner residual vortices. In the shallow water in fig. 7 these are nearly as long as the trough, and reach nearly to the top of the water. In the deeper water in fig. 9 they do not extend so far along the trough nor to the top of the water, and yet they are about the same height as those in fig. 7. In fig. 10, where the water is still deeper, the inner vortices do not occupy more than about half the length of the trough, and are only about a third of the height of those in fig. 9.

It seemed just possible that, if the water were made considerably deeper than half a wave-length, such vortices as F and F' (fig. 5) might spread along to the middle of the trough—to the loop—and become important. No such thing happens, however; it is difficult, even when the oscillations are very violent, to get any motion at all in the water lower down than half a wave-length, and the small corner residual vortices never spread *under* the outer ones; they rise a little higher, perhaps, as the water is deepened, but they remain always feeble and always in the corner, with their lower boundaries on a level with those of the outer vortices, and below this there is no apparent residual motion at all. Practically, then, in water as deep as, or deeper than, half a wave-length, the residual vortices are reduced to a single pair, of which the upper portion moves from loop to node and the lower from node to loop, and this single pair always extends to the top of the water, but moves over a layer of still water at the bottom, when the depth of the water is much more than half a wave-length.

It is interesting to notice that, whatever the depth of the water may be, in consequence of the way in which the outer residual vortices enclose the inner ones, the direction of the residual motion on top is always from loop

to node, that at the bottom from node to loop, and that at the nodes downwards (save for the small corner vortices). At the loops, on the contrary, although the residual motion of the upper part of the water is invariable, namely, vertically upwards, that of the lower part depends on the depth of the water, being downwards for any depth less than half a wave-length, and upwards—moving in the same direction as the upper part—when the depth is greater than this. Mathematically speaking, I suppose, there is always an infinitesimally small pair of inner vortices, and, therefore, a small downward current between the bottoms of the two outer vortices, however deep the water may be, but practically in water as deep as, or deeper than, half a wave-length these do not exist.

Fig. 11 is a photograph of water, permeated with bronze powder, which had been oscillated in half a stationary wave some half dozen times only, it shows clearly where the residual motion first becomes perceptible, viz., at the top of the water, at the nodes; for there is no apparent disturbance anywhere else.

The friction of the water against the front and back of the trough causes the residual motion to be slowest close to the glass and greatest half way between the front and back. This gives to the water-colour stain, that shows the residual motion in each quarter wave-length, a shape as of a sail bellying in a wind, which drives from the end of the trough towards the middle. The effect can be seen to a certain extent in α (fig. 9), but is much more clearly visible in the actual experiment.

One final feature of residual motion, that is rather curious, must be mentioned. It has been said that, after the oscillations have been stopped, the residual motion continues, and is even more apparent, owing to the cessation of the to-and-fro movement. In a short time, however—perhaps a minute after the oscillations have ceased—a part of the water begins to move in the opposite direction to that which it had previously taken, and this tendency gradually spreads till the whole motion of the liquid is reversed, though it is more confused than it was before. Where originally there was upward movement, there is now downward, and *vice versa*; motion from right to left has become motion from left to right, and so on. It is as if a set of water springs had been wound up, and now proceeded to unwind themselves.

To sum up the results of this investigation; the residual motion of water moving in stationary waves takes the form of two principal sets of vortices in each half stationary wave—the outer ones extending from loop to node at top and bottom, but embracing the inner ones in the middle—the inner pair, entirely surrounded by the outer pair, having their largest part at a loop,

and tapering to points near the bottom, between this loop and the corresponding nodes. Both the length and the height of the inner pair depend on the depth of the water, the length diminishing steadily as the depth of the water increases, and the height increasing till the depth of the water is about one-eighth the wave-length, and then diminishing till the water is as deep as half a wave-length, when they are practically reduced to nothing.

The outer pair of vortices, since they entirely surround the inner ones, naturally grow as these diminish, until at last, when the depth of the water is half a wave-length and the inner vortices cease to exist, the whole length of the half wave is occupied by two oblong residual vortices moving from loop to node above and from node to loop below, the vertical motion being upwards at the loop and downwards at the node.

On the Perception of the Direction of Sound.

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The following paper contains an account of a series of experiments on the perception of direction of sound which were undertaken with the object of investigating the nature of the influence of phase differences between the vibrations at the two ears. Lord Rayleigh* has shown that such differences help to determine the apparent direction of the sound, the sound appearing to be on the side at which the phase is the more advanced. Professor More† arrived at a similar conclusion to Lord Rayleigh by experiments of a different character. The following paper also contains a theory of the influence of phase differences which appears to offer a possible explanation of the observed effects.

Most of our experiments have been done with an apparatus similar in principle to Professor More's, but permitting of a continuous variation of the difference of phase. The apparatus consisted of a brass tube, AB (fig. 1), about 250 cm. long and 2·5 cm. in diameter, with a short T-piece soldered on to it at its middle point. This tube could slide freely in two slightly larger brass tubes, CD and EF, which were supported horizontally a definite

* 'Phil. Mag.,' February, 1907.

† 'Phil. Mag.,' April, 1907.

distance apart. From the ends of CD and EF wide tubes were led to caps fitting on to the ears of the observer. The tubes were made up of lengths of

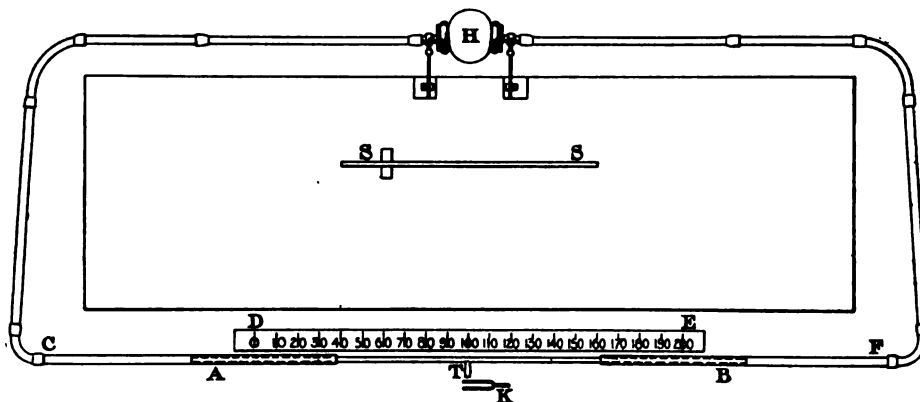


FIG. 1.

AB. Sliding tube.
DE. Scale.
T. T-piece.
K. Tuning fork.

CA, BF. Fixed tubes.
H. Observer's head.
SS. Screen on table.

glass tubing joined together by pieces of wide indiarubber tubing, and the two sides of the apparatus were made as symmetrical as possible. The ear caps consisted of wooden discs with annular soft pads round them which could be pressed against the head. The caps were supported on retort stands clamped to a table, and were adjusted as symmetrically as possible.

A graduated scale was fixed alongside the brass tube AB so that the position of the T-piece could be read off on it. A wooden screen was put up on the table between the observer and the T-piece, so that whichever way he was facing he could not see the position of the T-piece.

A vibrating tuning fork was held near the mouth of the T-piece so that some of the sound from it entered the tubes and went along them to the observer's ears. By sliding the tube AB about, any desired difference could be produced between the paths to the two ears.

Let the distance of the T-piece from the middle point (scale reading 100) of the scale be x cm., and the wave-length of the sound given out by the fork be λ , then the phase difference (α) between the sounds at the observer's ears is $4\pi x/\lambda$. If n is the number of vibrations per second and v the velocity of sound, then

$$\alpha = \frac{4\pi x}{\lambda} = \frac{4\pi n x}{v}.$$

According to Lord Rayleigh's results we should expect that for values of x between 0 and $\frac{1}{4}\lambda$ the sound would appear to be in the ear on the right

hand side of the middle point, while with x between $\frac{1}{4}\lambda$ and $\frac{1}{2}\lambda$ it would appear to be on the left, and so on for other values of x . If we denote the lateral effect by ϕ , and consider right effects positive and left effects negative, the connection between ϕ and x should be, according to Lord Rayleigh's results, $\phi = A \sin(4\pi nx/v)$, where A is a constant. It would, perhaps, be more correct to say that ϕ should be equal to a Fourier's sine series, of which the above is the first term, but experiment shows that the other terms are probably unimportant, if they exist at all.

One of us acted as observer while the other placed the T-piece in a series of positions, in each of which the observer said on which side the sound of the fork appeared to him to be. A record of the results was kept, and the series of observations was usually repeated. The sensations were usually described as follows:—"Full right," "half right," "middle or half right," "middle," "middle or half left," "half left," "full left." "Half right" meant that the perception of direction was only moderately definite, while "middle or half left" meant that there was only a doubtful perception of direction. "Middle" meant that the sound seemed to come from in front or behind, or that there was no lateral effect.

The following is a typical series of observations:—

Fork 512. Observer facing away from fork.

Scale reading.

| | | | |
|-----|-------|---------------------------|---------------------------|
| 100 | | M (1) | |
| 105 | | R (2) | R (26) |
| 95 | | L (3) | L (25) |
| 90 | | L (4) | L (24) |
| 110 | | R (5) | R (23) |
| 85 | | L (6) | L (22) |
| 80 | | L (7) | |
| 115 | | L (8) | L (21) |
| 120 | | L (9) | L (20) |
| 125 | | L (10) | L (19) |
| 75 | | R (11) | R (18) |
| 70 | | R (12) | R (17) |
| 130 | | M (13) | L (16) |
| 65 | | M or $\frac{1}{2}$ L (14) | M or $\frac{1}{2}$ L (15) |
| 135 | | R (27) | M or $\frac{1}{2}$ R (34) |
| 140 | | R (28) | R (33) |
| 145 | | L (29) | M or $\frac{1}{2}$ L (32) |
| 150 | | L (30) | L (31) |

The numbers in brackets indicate the order in which the observations were made.

The results obtained can be conveniently represented by means of curves whose co-ordinates are the scale readings showing the position of the T-piece and the lateral effects. The lateral effect corresponding to any scale reading was calculated by taking the mean of the observations at that point, counting a "full right" = 1, a "half right" = $\frac{1}{2}$, a "middle or half right" = $\frac{1}{4}$, a "middle" = 0, with equal negative numbers to represent left effects.

Fig. 2 shows one of the curves obtained in this way with a fork of frequency 512. The curve $\phi = \sin(4\pi nx/v)$ is also shown (dotted) and it will be seen that the observations agree with it as well as could have been expected.

Figs. 3 and 4 show similar curves obtained with forks with frequencies 384 and 128.

Fig. 5 shows some of the results obtained with frequency 256.

It will be seen that with frequency 256 the observed and theoretical curves do not agree, in fact the observed lateral effect is just the reverse of that expected.

A good deal of time was spent in investigating the cause of this anomaly and it was finally found to be due to resonance occurring in the tube on one side or the other, according to the position of the T-piece. The observer's ears were replaced by the thin indiarubber diaphragms of two manometric flames, which were observed in a rotating mirror in the usual way. In this way it was possible to compare the amplitudes of vibration on the two sides of the apparatus. It was found that the two amplitudes were always sensibly equal with frequencies 512 and 384, but with 256 there were large differences between the two amplitudes in certain positions of the T-piece. In fact, with this frequency, when the sound appeared to be on one side, there was a greater intensity of sound on that side, which evidently completely masked the phase difference effect. These differences of intensity could be detected, though not very certainly, by listening first at one tube and then at the other.

It was found that the same cause led to the discrepancy between the observed and calculated results with frequency 128 at $x = -60$ (see fig. 4). The lateral effects observed with frequency 256 were of precisely the same character as those observed with frequency 512, although it appears that the 256 effects were due to a difference between the sound intensities at the two ears, while those with frequency 512 were produced by a difference of phase without any difference in intensity.

Some experiments were tried with the tube on one side partially block

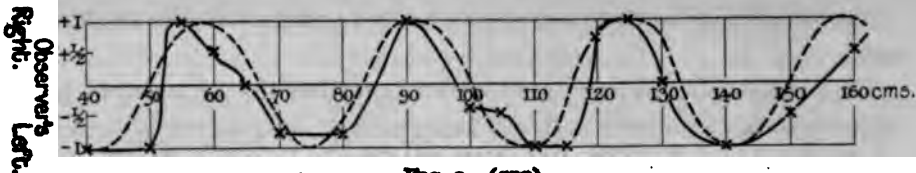


FIG. 2. (512)
(Observer facing towards fork)

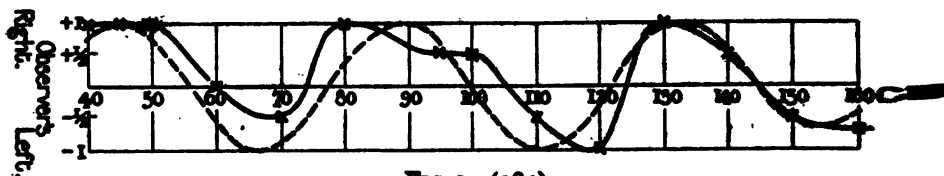


FIG. 3. (384)
(Facing towards)

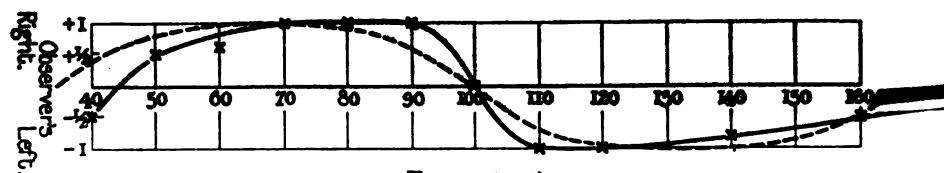


FIG. 4. (128)
(Facing towards)

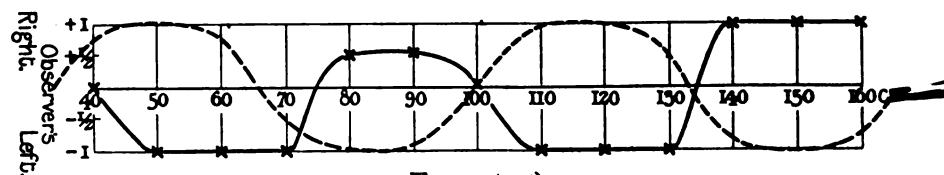


FIG. 5. (256)
(Facing away)

with cotton wool so that the sound on that side was considerably weaker than that on the other side. It was found that the observer, after a time, became accommodated, so to speak, to the difference of intensities, and lateral effect in both directions could then be obtained, although the sound was all the time stronger on one side than on the other.

Experiments were tried in which one side of the tube was gradually closed

(by means of a screw pinch-cock), and it was found that the observer did not notice any change in the lateral effect until the tube was almost completely closed, when, of course, the sound always went over to the open side. The sensation of change of direction produced in this way was precisely similar to that obtained by sliding the T-piece along with both tubes open.

Experiments were tried with tubes of different lengths and with the observer facing towards the fork and then away from it, but no very interesting results were obtained. Experiments were also tried with the manometric flames to see if the phase differences calculated actually existed, and this was found to be the case with frequency 256 as well as the others.

The results obtained suggest that while a difference of phase may be a primary cause of lateral effects, yet it acts by producing a difference between the intensities of the sound inside the ears. If we suppose that some of the sound entering an ear gets across through the head to the opposite internal ear, this enables a simple explanation of the phenomena to be given.

Let $y_1 = a \sin(\omega t + \alpha)$ denote the vibration entering the right ear, and $y_2 = a \sin \omega t$ denote the vibration entering the left ear. The resulting effect at the right internal ear will be, say,

$$y_1' = fa \sin(\omega t + \alpha) - ga \sin(\omega t - \beta).^*$$

Here f and g are proper fractions, of which f is much greater than g , and β is the retardation in phase due to the passage through the head.

In the same way, the effect at the left internal ear will be

$$y_2' = fa \sin \omega t - ga \sin(\omega t + \alpha - \beta).$$

Hence

$$y_1' = \{f^2a^2 + g^2a^2 - 2fga^2 \cos(\alpha + \beta)\}^{\frac{1}{2}} \sin(\omega t + \delta_1)$$

and

$$y_2' = \{f^2a^2 + g^2a^2 - 2fga^2 \cos(\alpha - \beta)\}^{\frac{1}{2}} \sin(\omega t + \delta_2),$$

where δ_1 and δ_2 are constants.

Let I_1 denote the sound intensity at the right internal ear, and I_2 that at the left internal ear. Then $I_1 - I_2$ is proportional to the difference between the squares of the amplitudes in y_1' and y_2' ; hence,

$$I_1 - I_2 \propto 2fga^2 \{\cos(\alpha - \beta) - \cos(\alpha + \beta)\} = 4fga^2 \sin \alpha \sin \beta.$$

Thus, the difference between the intensities at the two internal ears is proportional to $\sin \alpha$, and if we suppose that ϕ , the lateral effect, is proportional to $I_1 - I_2$, we get $\phi = A \sin \alpha$, where $A \propto 4fga^2 \sin \beta$, and so is a constant for sound of a particular frequency.

* We suppose that the displacements in the internal ear due to the two sets of waves are in opposite directions. It should be said that the principal reason for making this assumption is that it enables an explanation of the lateral effects to be given.

Thus, provided $\sin \beta$ is positive, if the phase at the right ear is ahead by an amount between 0 and π , ϕ is positive, that is, $I_1 > I_2$, and the sound will appear to be on the right side, whereas if α is between π and 2π , $I_2 > I_1$, and the sound will appear to be on the left side. Thus, the theory here proposed gives a complete explanation of the observed lateral effects due to phase differences. For very high-pitched notes β would be between π and 2π , and then the lateral effect would be reversed.

The distance between the ears through the head is small, and the velocity of sound through the bones probably very high, so that we should not expect a reversal of the effect due to this cause, unless the frequency were very great. But with very high frequencies the lateral effects cannot be obtained.

The amount of sound which must get through the head to produce an appreciable difference between the intensities at the two internal ears is not large, because since the two amplitudes are added, an imperceptible amount getting through might produce an appreciable difference of intensity.

It was found that an appreciable amount of sound could be sent through a person's head from one ear to the other. Ear caps with tubes attached were fitted to each ear, and a vibrating tuning fork was held near the end of one tube. An observer listened at the end of the other tube, and with a fork of frequency 512 a distinct sound was heard, which seemed to come along the tube. The amount of sound getting through the head must, of course, be much smaller than the amount entering one ear and getting to the opposite internal ear.

The experiments described were carried out in the Physical Research Laboratory at King's College, which has been fitted up with a grant of £500 from the Drapers' Company, to whom, therefore, we wish to express our obligations. We also desire to express our best thanks to Lord Rayleigh for his kind interest in the experiments and for some valuable suggestions.

*On the Intimate Structure of Crystals. Part VI.—Titanic Oxide,
its Polymorphs and Isomorphs.*

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The key to crystalline structure is furnished by a study of molecular volumes, and one of the best criteria of its powers will be found in its application to polymorphous compounds. If it can explain consistently with our knowledge of crystalline symmetry the change in volume which accompanies the passage of a substance from one crystalline system to another, this fact alone would seem to offer presumptive evidence in its favour. There are inherent difficulties in the subject which render progress laborious and slow, so that we cannot at present offer an exhaustive account of all cases of polymorphism, and on this occasion we shall confine our attention to the single but remarkable instance of titanic oxide, which presents itself in the three well-known forms of anatase, brookite, and rutile.

The chemical formula of the oxide, generally taken as Ti_2O_4 , is based on analogy with zircon, ZrSiO_4 , which is isomorphous with rutile. It may be

represented graphically as $\text{Ti} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \\ \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{Ti}$, and the simplest glyptic rendering of

this gives at once the general configuration of the crystal molecule, Haiiy's "molecule intégrante," out of which anatase, and, with slight modifications, brookite, and rutile also, are built up (see fig. 10, p. 275).

To obtain the molecule in its true relative dimensions, we must first determine the relative sizes of its constituent atoms. The gross atomic volume of metallic titanium is 13.4. This follows from the relation $mw/d = mv$, the molecular weight (mw) being 47.9, and the density (d) 3.5888. On the assumption that the atoms in titanium are arranged in open cubic order, this gives as the diameter of the atom 2.375, or radius (R) = 1.1875.

The gross atomic volume of oxygen cannot be obtained directly from the free element, and it is difficult to arrive at a completely satisfactory result from its compounds; in commencing this investigation, I selected the number 5.5 as representing an average of considerable probability; this gives for the diameter 1.765, or radius (r) = 0.8825. In an earlier part of

this paper* I made use of a somewhat higher value (1.89), but it is possible that the dimensions of the oxygen atom are not absolutely constant throughout all its combinations. In any case, the number 1.765 is that which harmonises with all the facts presented by the minerals we are about to consider.

Anatase.—The fundamental molecule of anatase consists of four atoms of oxygen arranged in contact, with their centres situated at the corners of a square: one atom of titanium rests upon the four oxygen atoms, its centre lying vertically above the centre of the square; the other atom is situated in a corresponding position below. On joining the centres of the titanium with those of the oxygen atoms, we obtain a pyramid of the tetragonal system, having an obvious resemblance to the primitive pyramid, which is the characteristic form of anatase.

These molecular pyramids may be built up into a crystalline edifice by arranging them so that the oxygen atoms lie in square order in one sheet, taken as horizontal (fig. 1); the titanium atoms form corresponding sheets

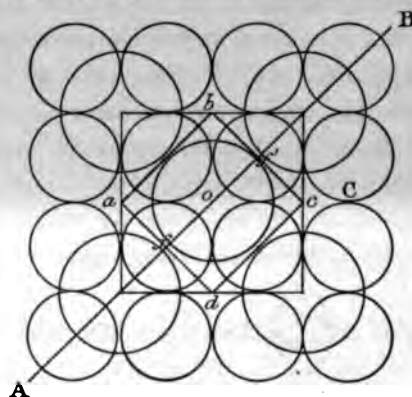


FIG. 1.—Anatase—Plan.

The larger circles in all the figures represent titanium, the smaller, oxygen atoms.

above and below. On this layer of molecules a second may be superposed in such a manner that the titanium atoms of its lowest sheet rest upon those sets of four oxygen atoms which are formed by the four corner atoms of four squares in contact below (fig. 2).

The structure thus obtained is tetragonal and holohedral; it may be regarded as a tetragonal lattice with the centres of the molecules situated on the nodes.

The packing is fairly close: to determine the volume occupied by one molecule of titanic oxide (taken for convenience as TiO_2), we must now partition the space occupied by the configuration homogeneously. In plan

* 'Roy. Soc. Proc.,' vol. 59, p. 294, 1902.

(fig. 1) the structure may be completely divided into equal square areas, such as $a b c d$, each including one atom of titanium and four half-atoms of oxygen; the length of the side is $2r\sqrt{2}$, and this squared gives $8r^2$, or 6.23.

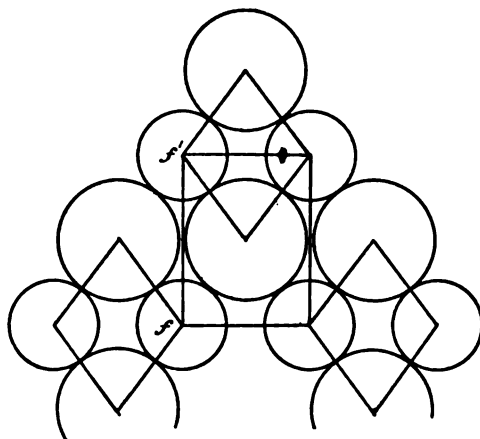


FIG. 2.—Elevation on a Plane passing through A B of fig. 1.

Each square again is the base of a tetragonal prism, which contains one atom of titanium and eight quarter-atoms of oxygen, in all one molecule of TiO_2 ; its height is shown by the line $f f'$ in fig. 2, and is measured by $\sqrt{(2R + 2r)^2 - (2r\sqrt{2})^2}$, or 3.303; the volume of the prism is therefore 6.23×3.303 , *i.e.*, 20.58. The best determinations of the specific gravity of anatase vary from 3.83 to 3.9, and its molecular volume lies consequently between 20.51 and 20.86, with a mean of 20.68. The accordance between the observed and calculated volumes is thus remarkably close.

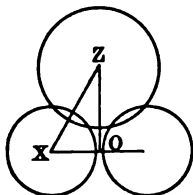
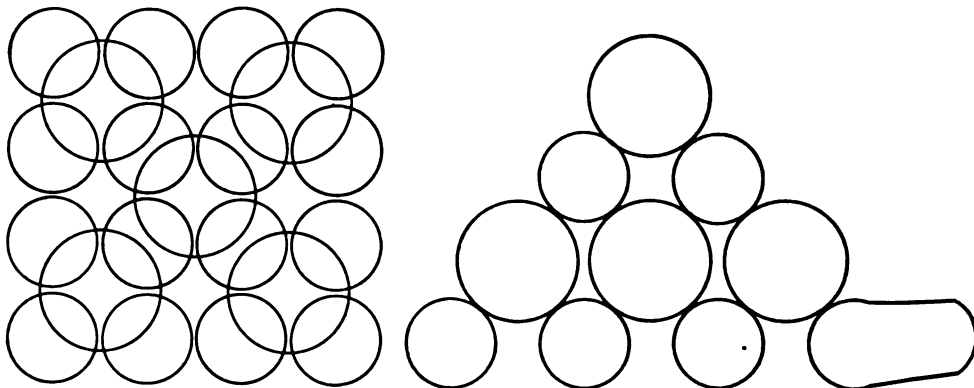


FIG. 3.—Elevation on a Plane passing through $a c$, fig. 1, but with the Oxygen Atoms separated as in fig. 4.

It is evident that the configuration we have described affords data for calculating the axial ratios or parameters of the crystal. For our horizontal axes we may select either oA or oC ; we take the latter and make the parameter equal to $2r$, the corresponding parameter on the vertical axis is given by the length of the elementary prism from which the volume was calculated; we have, therefore, for the horizontal parameter a length of 1.765, and for the vertical of 3.303, and this gives a ratio of 1:1.871, while

the ratio obtained by direct measurement of the mineral is 1:1.778. The agreement in this case is only roughly approximate. We may make it a little closer, however, by slightly modifying our original conception of the molecular configuration; we have supposed the oxygen atoms to lie in contact with each other, let us now separate them by a short interval; this will allow the titanium atoms to approach one another, and the total effect will be to lengthen the horizontal parameters and shorten the vertical parameter, at the same time the volume will be increased (figs. 4 and 5).



FIGS. 4 and 5.—Similar to figs. 1 and 2, but readjusted into a nearer approximation with the actual axial ratios of Anatase.

In determining the amount of the change which can be produced without unduly increasing the molecular volume, we shall make use of the horizontal axes we have already chosen do not correspond with the sides of the square which forms the base of our elementary prism; we must compensate for this by changing the axial ratios from 1:1.778 to $1 \times \sqrt{2} : 1.778$ or 1:1.2572. For the volume we take the mean, 20.6

Then, since $\chi = \sqrt[3]{\frac{a_1^2 V}{c}}$, we have $\chi = \sqrt[3]{\frac{20.68}{1.2572}} = 2.5431$, and $\omega = c\chi$

$2.5431 \times 1.2572 = 3.183$. Thus the parameters on the topical axes are 2.543 and 3.183; and from χ we obtain the corresponding parameter on a by dividing by $\sqrt{2}$, which gives 1.7983; but $2r = 1.765$, and thus the interval between adjacent oxygen atoms amounts to 0.033.

With the data at our disposal, we can now calculate the length of the vertical parameter as given by our configuration when modified by the separation of the oxygen; it is found to be 3.267, while the topical axes show it to be actually 3.183, a difference of 0.084, or about 2½ per cent.

* According to Schrauf's measurements the axial ratio of anatase is 1:1.784; this gives 3.205 for ω , and our value deduced from the configuration becomes 3.27, or a difference of 2 per cent.

Our results, however, are based on the improbable assumption that all atoms possess a spherical form, and are thus first approximations only. It is extremely likely that the atoms of those elements which crystallise in other systems than the cubic are not true spheres. The analogy of oxygen with sulphur and of titanium with tin suggests that this may be the case with the atoms under consideration.

Anatase cleaves readily along the planes of (111) and (001). But it may be observed here that the form (111) does not correspond to the form of the integrant molecule: the symbol for this, according to the axes we have chosen, must be (101). The primitive pyramid of the crystallographer only arises when the molecules are built up into the crystalline edifice; its basal section is given in the square *ac* of fig. 1. The connection between cleavage and structure is thus not immediately obvious, but on referring to the diagram (fig. 1) it will be seen that alternate squares of four oxygen atoms exist over which titanium atoms are absent, both above and below, and these unoccupied spaces run in files parallel to the horizontal edges of the pyramid (111), all the other squares being covered with titanium atoms. It would seem probable that the structure should part along these lines in preference to any other. The basal cleavage (001) follows readily from the structure.

The optical sign of anatase is negative, $\omega = 2.554$, and $\epsilon = 2.493$; hence the axis of greatest elasticity corresponds with the principal axis of the crystal, or the titanium axis of the molecule.

The coefficient of thermal expansion is greatest along the principal axis, least along the axes normal to it. According to Fizeau, it is 0.0819 parallel to *c*, and 0.0468 in any direction normal to this; according to Schrauf, it is 0.0664 in the first direction, and -0.0288 in the second. To this relation we shall recur later.

Rutile.—Although rutile crystallises in the same system as anatase, it presents very different forms, and cannot be referred to the same axes. Its fundamental molecule has the same constitution as that of anatase, i.e., there is no polymerism; but it differs in two respects: first the titanium atoms have approached each other along the vertical axis so far as to come into contact; and next, as a consequence, the oxygen atoms have been pushed outwards as far as possible, so that they lie comparatively far apart, though still at the corners of a square, having its plane at right angles to the vertical axis, which passes through its centre and the centres of the two titanium atoms above and below (fig. 10).

The arrangement of these molecules differs completely from that which obtains in the case of anatase. The first layer is formed by placing the molecules with the titanium axes horizontal and end to end, so that the

titanium atoms form continuous horizontal files; on bringing these together side by side they will be found to fit together, the molecules of adjacent files alternating with each other. The titanium atoms are thus marshalled in square order in a single sheet, and the oxygen atoms lie one over the centre of each square of four titanium atoms, forming two sheets, one above and one below (fig. 6). If the bonding of the atoms be disregarded, this configuration will be tetragonal; but when the bonds are taken into account it becomes rhombic; consequently, to preserve the tetragonal character, the next layer of molecules, which is built up like the first, must be turned in a horizontal plane through an angle of 90° , and then superposed so that the two titanium

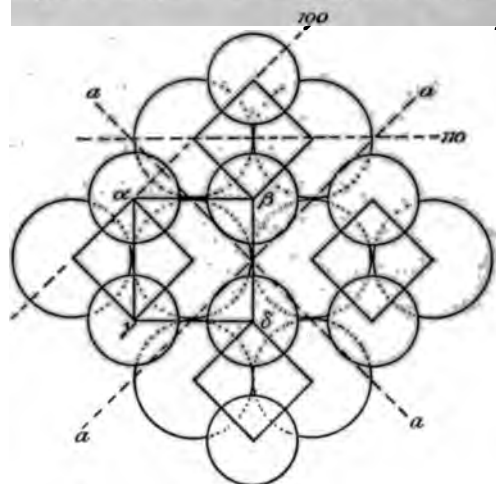


FIG. 6.—Rutile—Plan.

atoms of one molecule lie immediately over the two oxygen atoms of the layer beneath, the centres of the two molecules lying on the same vertical axis (figs. 7 and 8). The structure so produced is tetragonal and holohedral; the

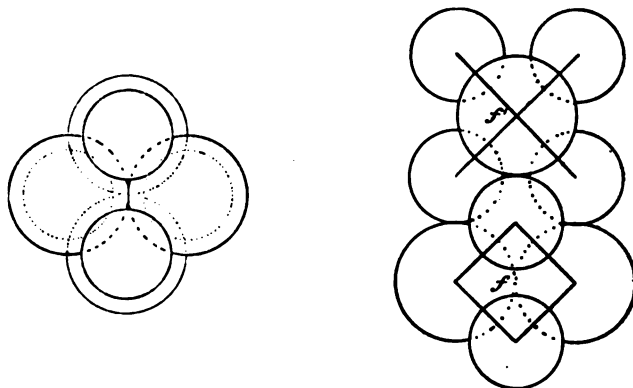


FIG. 7.—Plan of Two Molecules superposed. FIG. 8.—Elevation on Face 110.

gyrohedry, since it amounts to a right angle, having no crystallographic effect.*

We may partition the structure homogeneously into square prisms, having as a base the square $\alpha\beta\gamma\delta$ of the figure (fig. 6) with an area of $(2R)^2$, or 5.6406; the height is shown by the line ff' (fig. 8), and nearly equals $2R + \tau$,† or 3.2575. The volume is, therefore, 18.375. The specific gravity of rutile lies between 4.2 and 4.3, and its molecular volume between 18.6 and 19, but when heated in hydrogen the specific gravity rises to 4.365, or the volume diminishes to 18.305. The agreement between theory and observation is thus as close as we can expect.

If we take the height of the prism just determined (3.257) as the vertical parameter of the crystal, then the horizontal parameter will be $\frac{2}{3} \times 2R\sqrt{2}$, or 5.0831, and the ratio $5.0831 : 3.28 = 1 : 0.6442$. The actual ratio found by angular measurement of the crystal is $1 : 0.6442$.

The most perfect cleavage of rutile is parallel to the prism faces (110), a fact consistent with the configuration; there is a cleavage parallel to the faces of the second prism (100) also, but this is less perfect than the preceding, though there is nothing in the configuration which would have enabled us to predict this fact.

Rutile exhibits a characteristic tendency to form greatly elongated prisms, and this is quite in harmony with the configuration, which presents a much closer texture over the prism faces than at right angles to them, that is to say, the surface density is greater parallel to the axis c than in any other direction.

The optical sign of rutile is positive, and consequently the direction of greatest elasticity corresponds with the horizontal axes of the crystal, but it is along these axes that the titanium axes of the molecules are disposed, so that we have in this case precisely the same relation as that which we found to obtain in anatase.

In agreement with the optical characters, the dielectric constant is at maximum parallel to the principal axis, its value in this direction being 73; at right angles to it only 89, or about one-half. If the truth of our configuration should be confirmed, this ratio should afford some insight into the difficult question of the connection between the optical properties and the molecular structure of a crystal.

The thermal conductivity is at a maximum parallel to the principal axis.

The thermal expansion, as determined by Fizeau, gives a coefficient for the

* Schrauf, however, has observed gyrohedry in some crystals of rutile: it would appear, therefore, that the rotation is not always complete.

† The error introduced by this formula only affects the fifth place of decimals.

vertical axis of the crystal of 0.0,919, and for the horizontal axis of 0.0,714; if the volume of the oxygen atom expands to a greater extent than that of the titanium atom for the same rise of temperature, this relation between the coefficients is such as the configuration might lead us to expect.

It not infrequently happens that prisms of rutile occur "attached to plates of hæmatite in such a position that each prism lies with its face (100) upon the basal plane of the hæmatite, and with its prism edge perpendicular to the edge of the combination (111):(100) of the hæmatite, fig. 220."*

Some light seems to be thrown on this interesting phenomenon by the structure of the two minerals; an attempt to formulate the structure of hæmatite shows that the atoms on the basal plane lie on the nodes of a hexagonal network; and when the structure we have assigned to rutile is observed as it presents itself on the side of the prism (100), it also is found to exhibit a hexagonal arrangement, which, although not quite regular, may perhaps be sufficiently so to allow of the co-adjustment of the two crystalline structures (fig. 9).

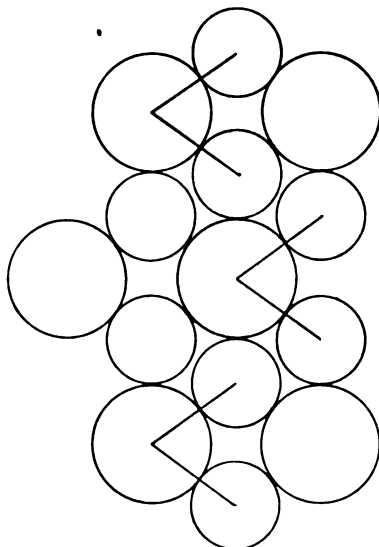


FIG. 9.—Elevation on Face of the Prism (100).

Brookite.—This mineral crystallises in the rhombic system. Its molecule has the same chemical formula as anatase and rutile, and there is no polymerism. The titanium atoms have approached each other and come nearly but not quite into contact, and the oxygen atoms, though pushed out, are not equally separated, but lie at the corners of a rectangle having two sides longer than the others. Thus the molecule itself possesses a rhombic

* 'Mineralogy,' by Professor Miers, 1902, p. 86.

form, which is therefore inherent in the crystal from the first; in the same way the tetragonal form is already determined in the molecule in both anatase and rutile. The difference between the three molecules will be seen by inspection of fig. 10, which represents them in plan.

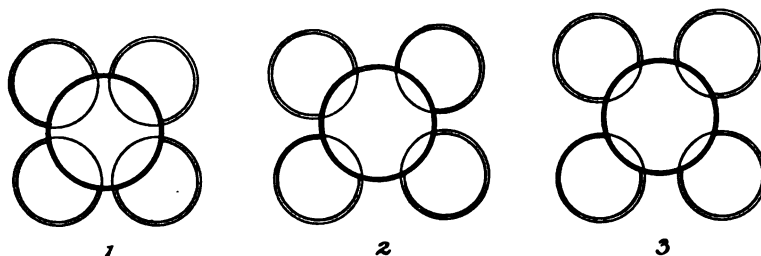


FIG. 10.—Molecules of Anatase (1), Brookite (2), and Rutile (3), shown in Plan.

The first layer of molecules is constituted very much as in rutile, but with this difference that the adjacent files of titanium atoms are not in contact with each other, but separated by intervening oxygen; they form a rectangular but not a square lattice (fig. 11).

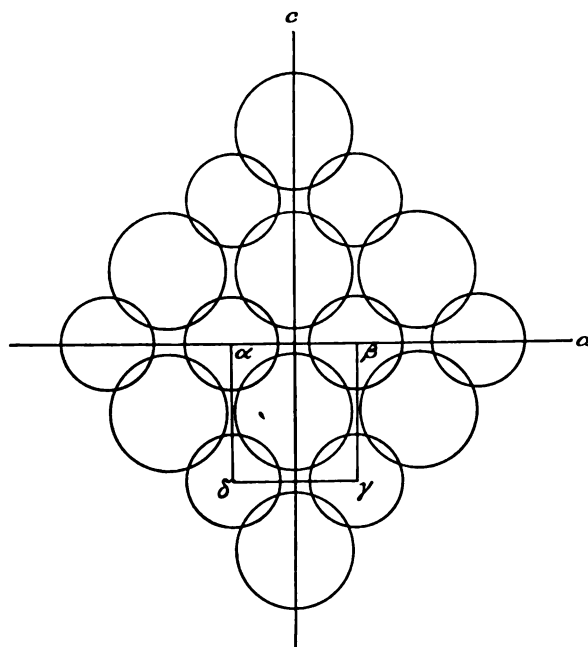


FIG. 11.—Plan of First Sheet of Molecules.

The second layer of molecules has the same constitution as the first, and is superposed with the same orientation, but with a slight horizontal displacement parallel with the axis c , so as to bring the oxygen atoms of the upper

layer immediately over the interspaces between the most closely approximated titanium atoms of the layer below (fig. 12). The third layer is similarly superposed, but with a compensatory displacement in the opposite direction.

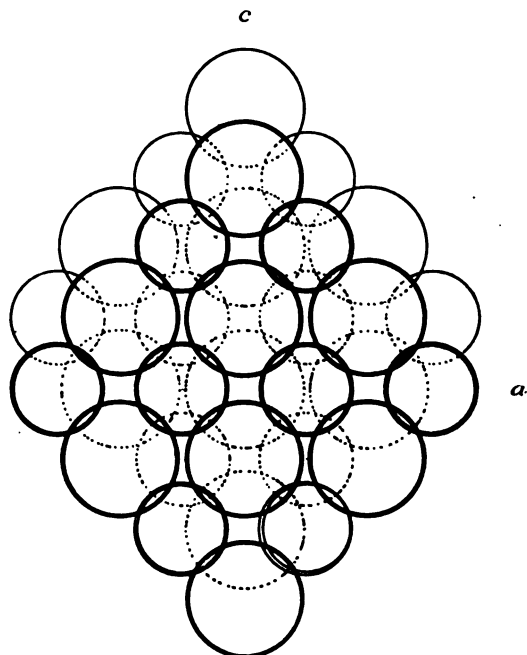


FIG. 12.—Plan of Two Sheets of Molecules.

The structure so produced fulfils all the conditions of rhombic symmetry.

The simplest means of testing this hypothetical configuration is furnished by the so-called topic axes. The specific gravity of brookite ranges from 3.9 to 4.2, but the most probable value lies near 4.0.* This gives for the molecular volume 19.975. The accepted ratios of the parameters are 0.841:1:0.944. The topic ratios are, therefore, as follows:—

$$\chi = \sqrt[3]{a^2V} = 2.4644; \psi = \chi/a = 2.9304; \omega = c\psi = 2.7661.$$

In our construction (fig. 11) we make the sides $a\beta$ and $a\gamma$ of the rectangle $a\gamma$ equal to 2.4644 and 2.7661 respectively, but we now proceed to determine the vertical parameter by means of the diameters of our atoms, and we obtain as a result the number 2.9468, while the observed value is 2.9304, or a difference of 0.0164, *i.e.*, about 0.5 per cent. This is the sole difference which exists between the results obtained by hypothesis on the one hand and observation on the other. The volume is only slightly affected, still remaining well within the limits of its observed values.

* Miers, 'Mineralogy,' p. 365.

The refractive indices for sodium light are: α , 2.5832, β , 2.5856, γ , 2.7414. The acute bisectrix coincides with the axis a and is positive; thus the direction of maximum elasticity coincides with the axis c , or with the titanium axis of the molecule, precisely as it does in both anatase and rutile.

The thermal expansion has been studied by Schrauf, who obtained the following coefficients at 17° C.: a , 0.041449; b , 0.04192; c , 0.042205.

We may here return to the question of thermal expansion in connection with all the members of this polymorphous series.

There are at least three ways in which changes of temperature may affect the relative dimensions of a crystal. Confining our attention to a rise of temperature, this may act: (1) by enlarging the space dominated by one set of atoms, oxygen, for instance, to a greater extent than that of the others. This will account for the relative changes in the length of the axes in the case of rutile, where the question is not complicated by changes of configuration; but it is inapplicable to anatase, the coefficients of which are in the inverse order of magnitude to that which this change would produce; (2) In the next place, a rise of temperature might cause the atoms of one kind, say the oxygen, to become more remote from each other, allowing the other titanium atoms to make a closer approach. This is what, by hypothesis, must happen in the case of the molecules of anatase and brookite; but in this case also the change in the dimensions of the axes, at least in the case of anatase, is in the opposite relation to that found by observation. (3) There remains then the third factor: the rise in temperature may initiate those changes in the configuration by which ultimately one form passes into another. The final change may well be abrupt, but there would seem to be no good reason why preparatory movements may not be set up long before the final change.

Looked at from this point of view, the relative length of the topic axes in the several polymorphs might be expected to throw some light on the matter; they give the integral effect of the various changes along definite directions. In the following table the topic axes are compared, the c axis of rutile being homologised with the a axis of anatase:—

| | $a.$ | $b.$ | $c.$ |
|---------------|-------|-------|-------|
| Anatase | 2.543 | 2.543 | 3.188 |
| Brookite..... | 2.464 | 2.930 | 2.766 |
| Rutile..... | 2.380 | 3.257 | 3.257 |

The corresponding thermal coefficients are as follows:—

| | a. | b. | c. |
|----------------|---------------------|---------------------|------------------------------------|
| Anatase | 0·0,468 -0·0,288 | 0·0,468 -0·0,288 | 0·0,819 Fizeau 0·0,864 Schrauf. |
| Brookite | 0·0,145 | 0·0,193 | 0·0,230 |
| Rutile | 0·0,714 | 0·0,714 | 0·0,919 |

It will be seen that the a axis consistently diminishes throughout the series, and this is in harmony with Schrauf's observation of a negative coefficient, in the case of anatase. But the second a axis of anatase (b in the table) should give a positive coefficient. It is barely possible that it does so, and in this might be found the reconciliation between the apparently discordant observations of Schrauf and Fizeau. On the other hand, the complicated change which occurs in passing from anatase to brookite would seem to render it necessary to consider the axes b and c of brookite together, and to compare them with the second a axis and the c axis of anatase taken together. We then have for anatase $a \times c = 8·095$, and for brookite $b \times c = 8·105$, a very insignificant expansion.

Turning next to the relations between brookite and rutile, the topic axes suggest a contraction along the a axis, and an expansion along the axes b and c , but to a greater amount along c than b . In correspondence with this, we find that the expansion (instead of contraction) which takes place along a is represented by the minimum coefficient, and that the expansion along c is greater than along b .

Considering how many factors enter into the problem, this amount of agreement is as great as we can expect. It does not perhaps lend much confirmation to our hypothetical configuration, but relieves it from serious objections.

Using constant dimensions for our atoms, we have been able to build them up according to the strict laws of crystalline symmetry into the three forms characteristic of the different polymorphs of titanium oxide, we have obtained for our hypothetical configurations similar volumes and similar parametral ratios to those determined by observation, and we have shown how the properties of these configurations are in harmony with what is known of the thermal and optical properties of the minerals they represent. If, however, our speculations possess any basis of truth, we should be able not only to explain the polymorphs, but also the isomorphs of titanium oxide, such as tinstone and zircon, which crystallise in similar forms to rutile. I have not as yet sufficiently studied the volumes of silicon and zirconium, and must therefore confine myself for the present to tinstone.

The metal tin crystallises in the tetragonal system, and consequently its atoms are probably not true spheres, or, what possibly comes to the same thing, their poles are not of equal value. In the absence of information as to the parametral ratio of the crystals, it is impossible to estimate what amount of deviation from the spherical form exists; but we may expect to find some anomalies consequent upon it in studying the metal in its compounds. We have already had occasion to refer to one of these compounds* when we took for the diameter of the atom of tin the number 2·535, which we will again adopt. The specific gravity of tinstone lies between 6·8 and 7·1, and the molecular weight is 150·7; the volume ranges, therefore, from 21·2 to 22·5.

We imagine the crystal to be built up in precisely the same way as rutile. The area of the base of our elementary prism is consequently equal to $(2R)^2$ or $2·535^2$, *i.e.*, to 6·4262; the height is given approximately by the formula $2R + r$, which is correct to the fourth place of decimals; it amounts to 3·4175, and this multiplied into 6·4263 gives 21·96 as the volume found from the configuration: thus very nearly equal to the mean of the observed values.

The parametral ratio found from the configuration is 1:0·6355; while by observation it amounts to 1:0·672, a difference of 0·037. This is more accordant than might have been expected.

It may be pointed out that if molecular volumes assist us to understand crystalline structure, the converse is also true that crystalline structure throws some light on the anomalies presented by molecular volumes. Taken in the gross the volumes of the three forms of titanium oxide can only awaken distrust in the significance of atomic volumes; thus, if we deduct the gross atomic volume of titanium from the volumes of the dioxide in its several forms we have the following results:—

| | Ti. | O ₂ . | |
|-----------|-------|------------------|----------------------------------|
| Anatase | 20·6 | —13·4 = 7·2, | or volume of one atom of O, 3·6. |
| Brookite | 19·97 | —13·4 = 6·6, | „ „ 3·3. |
| Rutile... | 18·4 | —13·4 = 5·0, | „ „ 2·5. |

Thus, by this method, the volume of one atom of oxygen is found to be both inconstant and unduly low, but a study of the crystalline structure shows that the irregularity may be merely apparent, and restores us the oxygen with a constant and normal volume (5·5).

Before writing this account I was unaware that the subject had already been treated by previous writers; a valuable literature, however, exists.

* 'Roy. Soc. Proc.,' vol. 63, p. 297, 1898.

Schrauf has published some highly speculative views,* and attributes to rutile the structure we have assigned to anatase. Prior has made some suggestive remarks on the homologies of titanium oxide,† to which I hope to recur when treating further of the isomorphs of this substance. The work which most nearly touches my own is by Baumhauer,‡ who, restricting his attention to anatase, arrives at a similar molecular and crystalline structure to that advocated here, and he supports his conclusions by a variety of important arguments based on the crystalline form, and etch figures in relation to a Bravais net; but the atoms of the molecule are indicated by their centres only, and no attempt is made to discuss the question of molecular volumes.

* Albrecht Schrauf, "Ueber die Trimorphie u. die Ausdehnungskoeffizienten von Titandioxyd," 'Zeita. f. Kryst. u. Min.,' 1884, vol. 9, p. 433.

† G. T. Prior, "Molecular Volume and Chemical Composition," 'Min. Mag.,' 1902, vol. 13, p. 320.

‡ H. Baumhauer, "Die Krystallstruktur des Anatas," 'Zeita. f. Kryst.,' 1895, vol. 21, p. 555.

*Report on the Eruptions of the Soufrière in St. Vincent in 1902,
and on a Visit to Montagne Pelée in Martinique. Part II.—
The Changes in the Districts and the Subsequent History of
the Volcanoes.*

By Dr. TEMPEST ANDERSON.

(Communicated by Professor T. G. Bonney, F.R.S. Received January 11,—
Read January 23, 1908.)

(Abstract.)

This Report, and the accompanying Report by Dr. Flett on The Petrology of the Ejected Materials, form the sequel to the Report by Drs. Tempest Anderson and J. S. Flett on "The Eruptions of the Soufrière in St. Vincent 1902, and on a Visit to Montagne Pelée in Martinique, Part.I."

At the time when that Report was published it was contemplated that an account should be given later on of the subsequent changes in the deposits of volcanic ejecta, and also on the petrology of the specimens collected in 1902. In the spring of 1907 I visited the West Indies, but Dr. Flett was unfortunately detained in England by his official duties. I am therefore unable to make possible for the field observations on the topography and geology, and on the return of vegetation, while Dr. Flett's Report deals with the petrology of the ejected materials.

A description of the topography of the Soufrière volcano and of the details of the immediate results of the eruption of 1902 are contained in the published Report, Part I. The principal points of interest in the observations made during my second visit lie in (i) the changes wrought by denudation on the deposits left by that eruption; (ii) the light thrown by those changes on the operation of the forces which had moulded the features of this island in its earlier history; (iii) the information I was able to collect with regard to volcanic disturbances subsequent to the great eruption of May, 1902; (iv) the return of vegetation to the devastated areas.

In the 1902 eruption a certain amount of the ejecta overtopped the Somma ridge, i.e., the remains of the original great crater, and descended some of the slopes to the north of it; but by far the greater portion was discharged into the transverse depression which extends right across the island and separates the Soufrière from the mountain known as Morne Garu, about three miles to the south. The water from the crater lake was discharged at the beginning of the eruption down the Rabaka and Wallibu rivers, while the solid and

gaseous ejecta, in the form of the incandescent avalanches and black clouds, descended to both sides of the island.

The most important geological phenomena were observed in the Wallibu district. These phenomena have been fully described in the published Report (Part I, p. 428 *et seq.*), as also the subsidence of part of the coast. To this district, therefore, attention was especially directed in 1907, with the view of observing the further progress of the changes and the return of vegetation.

A description of the Wallibu valley is given in the full paper. In this district the beds of newer date have been dissected into flat-topped plateaus by small rivers running in deep gorges, which have again been filled in place by ejecta of eruptions and re-excavated in different degrees, and sometimes on different lines, leaving plateaux and terraces of different ages and heights. This action is well exemplified in the lower Valley of the Wallibu. In the 1902 eruption this part of the valley was filled by the incandescent avalanche to a depth of at least 100 feet in the upper part, and less towards the sea, and it was in this deposit of hot ash that the explosions of steam and hot ash, flows of boiling mud and other secondary phenomena took place. In 1907 almost the whole of this ash had been washed away, but a fragment remained in the shape of a terrace 60 to 80 feet high, situated on the north side of the valley. The ash of which it is formed is unstratified, and contains very few ejected blocks or fragments of any kind. The floor of the valley is all composed of water-sorted material, chiefly gravel and coarse sand, but with a good many blocks as big as a man's head. They represent ejected blocks and fragments of lava derived partly from the ash of 1902 and partly from older beds, the fine ash in each case having been washed away. The surface of the gravel bed showed marks of quite recent running water, and during the last winter, 1906-7, the river ran along the foot of the north bank of the valley. When examined in March, 1907, it ran along the south side of the valley, and had already in those few months excavated a new channel about 30 feet in depth. The stratification, as exposed in the side of this new valley, is very distinct, and the sorting by water, mentioned above, is very evident. Further up the mountain the remains of the avalanche became more abundant in the valley bottoms, and here they were also often better preserved, so that traces of the feather pattern erosion, so noticeable in 1902, were still visible on the surface. This was mainly due to the surface of these ash deposits, like those to be presently mentioned on the plateaux and on the ridges, having consolidated into a crust almost like a cement pavement which resists the action of the rain.

Another interesting point was observed with regard to these massive ash deposits. Instead of one stream re-establishing itself along the centre of

the deposit, the tendency is for a new stream to form on each side at or near the junction of the new ash with the old valley slopes; and, as these streams deepen themselves, two new valleys are formed where only one previously existed, and the walls of each are composed on the one side of the new ash and on the other of older tuff, with occasional terraces of new ash. It appears to be due to the fact that the water from the old slopes, in running down into the original valley, meets the soft new ash, and at once turns down along the valley and so starts the new stream, and it seems likely that the chief cause of its so turning is that the surface of the deposit tends to be higher along the middle of the valley than at the sides, as is usual with mud-streams or glaciers. A good example of the action above described is to be found in a wide valley to the north of and parallel with the lower Wallibu valley and bounded on the south by the Wallibu plateau. Before the 1812 eruption the Wallibu river flowed down this valley, but its course was changed after that eruption. The floor of the valley is now occupied by the gorges of two small rivers, divided by a very narrow ridge, formed of ash different from and less consolidated than that composing the walls of the main valley, and considerably lower than the Wallibu plateau. In 1902 both these gorges were filled with new ash to the level of the main valley floor. One of these, the Trespé gorge, now emptied of the 1902 ash, shows its north wall to be much higher than the south, and also formed of older and more consolidated tuff. The same conditions, with sides reversed, are seen in the other gorge, the higher bank in that case being the Wallibu plateau to the south.

The Wallibu plateau is composed of ash older than that dividing the above two small rivers, but still comparatively new, and its flat top and precipitous sides, both north and south, proclaim it to be in an early stage of denudation, while the south bank of the Wallibu river on the south of the plateau is composed of older tuff and lava, and shows a much more mature type of denudation, viz., sloping hills with rounded or ridged tops, and a good deal weathered into valleys or gullies. The north face of the plateau, like the south, is precipitous and obviously much less advanced in weathering than the slopes of the Soufrière on the opposite side of the broad valley of the Wallibu Dry, and Trespé rivers to its north. The mass appears to be the remains of an avalanche, or succession of avalanches, of hot ash poured into the depression between the Soufrière and Morne Garu, on an enormously larger scale than anything formed by recent eruptions. It may be that the present bed of the Wallibu to the south and the broad valley to the north are enlarged and deeply-excavated developments of the valleys that were formed at the sides of this prehistoric avalanche.

Descriptions of the changes in the fans and low plateaux subsequent to 1902; of the shore subsidence; and of the upper slopes of the mountain, are given in the full Report, as well as a detailed description of the crater as seen in 1907. This is best explained by reference to the plates accompanying the Report.

The topography of the old crater is still correctly represented on the Admiralty Chart (published with the Report, Part I). The whole of the interior of the crater is still quite bare, without any trace of returning vegetation; small patches of moss appear about the rim and on the slopes outside, then grasses and herbaceous plants, and lastly, below a height of about 1500 feet, luxuriant tropical vegetation.

The present condition of the devastated areas is described fully in the Report, which contains also a history of subsidiary eruptions which followed the great one of May, 1902. The difference in character between the eruption of the Soufrière and Montagne Pelée, referred to in the Report of 1902, appears to have continued since that year, the outbursts from the former volcano being generally less frequent but more violent than from the latter.

The Report also contains an account of a subsequent visit to the volcano of Montagne Pelée, in Martinique, with a description of the crater as I then found it; a discussion of the phenomena of the remarkable extrusion and subsequent destruction of the Dome and Spine, which have been described by Lacroix and others, and a comparison of the sequelæ of the great eruptions in the two islands of Martinique and St. Vincent.

*he Observation of Sun and Stars made in some British Stone
Circles. Third Note.—The Aberdeenshire Circles.*

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(Received January 15,—Read January 30, 1908.)

previous communications to the Royal Society,* I have shown that if
nsider the sun's declination at the quarter-days of the May year and at
lstitices, and also the changes due to precession in the places of five or
the more conspicuous stars visible, at any epoch, in these latitudes we
le to account for the alignments investigated in the stone monuments
rnwall and Devon.

e present paper deals with a special class of circles in Aberdeenshire in
the method of indicating alignments shows a striking difference.
ornish method was that still set out in the instructions for the erection
e Gorsedd circle of the Welsh Eisteddfod,† the sighting, or directing,
s were placed some distance outside the circle. In Aberdeenshire the
od employed was to place a long, recumbent stone generally between
f the upright stones of the circle itself and to obtain the direction of
ising sun or star by sighting across the circle at right angles to the
h of the recumbent stone.

every case yet investigated, with two exceptions where there had been
rbance, I have found this sight-line to have had apparently the same
al direction, and therefore the same astronomical use as in Cornwall.

the tables, I give the name of the circle, followed by the magnetic,
th of the direction of the longest surface of the recumbent stone
ds E., as determined with a Barker clino-compass. Deducting
15'—the westerly variation of the compass in Aberdeenshire at the
nt time—from this, we obtain the true azimuth, which is given as
ned from N. through E. On deducting 90° from this, we get the line at
angles, which I believe to be the sight-line for which the circle was
ed; of this the true azimuth is also given.

e local conditions often militate against the exact determination of the
tion of the horizon, but, where possible, I measured it approximately
the compass-clinometer and state the results.

Roy. Soc. Proc., vol. 76, A, p. 177, March 15, 1905, and vol. 77, A, p. 465, March 19,

ee 'Nature,' vol. 76, p. 9.

The alignments are limited to four regions with about the following azimuths:—

N. 43° E. The sunrise at the summer solstice.

N. 59° E. The sunrise in May.

N. 5°—30° E. Clock-star observations.

True north.

I take them in this order.

Summer Solstice.

I found that three circles were probably erected to watch the summer solstice sunrise. The following table (I) shows the results of the measurements. With these circles accurate measurement is a difficult matter and, as the determination of the date of erection from the variation of the obliquity of the ecliptic entails very precise measures, I content myself with pointing out that the declinations are solstitial and that they agree, in the mean, with the values previously obtained for the English solstitial circles.

Table I.

| Circle at— | Azimuths. | | | Elevation of the horizon. | Declination N. |
|-------------------------|---------------------------------|--------------------------|--------------------------------------|---------------------------|----------------|
| | Magnetic, mean of observations. | True, from N. through E. | True, at right-angles across circle. | | |
| Sunhoney | ° / | ° / | ° / | ° | ° / |
| Midmar | 155 15 | 136 30 | N. 52 35 E. 46 30 | 4 | 22 25 |
| Stonehead (Insch)... .. | 146 15 | 127 30 | 37 30 | 2 | 23 15 |
| Mean of above... | ... | ... | ... | 1 | 25 41 |
| | | | | ... | 23 47 |

* * At Sunhoney, as the recumbent stone was curved and irregular, it was simpler to measure directly across the circle at right-angles to the length of the recumbent stone; the magnetic azimuth thus obtained was 71° 20'.

Table II.—English Monuments, for Comparison.

| Monument at— | Alignment. | Azimuth (true). | Elevation of the horizon. | Declination N. |
|-----------------------|------------------------------------|-----------------|---------------------------|----------------|
| | | ° / | ° / | ° / |
| Stonehenge | Direction of avenue from circle | N. 49 34 E. | 0 35 | 23 54 |
| Stanton Drew | Great circle to N. E. circle | 51 0 | 1 5 | 23 49 |
| Boscawen-Un | Centre of circle to fine menhir | 53 30 | 1 15 | 23 58 |
| Tregeseal | Centre of circle to holed stones | 53 20 | 1 15 | 23 2 |
| Longstone (Tregeseal) | To Mên-an-Tol..... | 50 30 | 0 34 | 24 7 |
| Mean of above ... | ... | ... | ... | 23 34 |

May-year. Sun's Declination 16° 20' N. (May 6, August 8).

If the circles, as shown in Table III, were apparently erected for the purpose of sunrise at the commencement of the May-year. A comparison of the results given in this table with those given in Table IV shows how they agree, in the mean, with the results obtained from the previous determination of May-sun alignments in Cornwall and Devon.

Table III.

| | Azimuths. | | | Elevation of the horizon. | Declina- tion N. | Dates. | |
|---------|--------------------------------------|--------------------------------|--|---------------------------------|------------------------|--------|---------|
| | Magnetic mean of observations. | True, from N. through E. | True, at right-angles across circle. | | | May. | August. |
| | ° | ° / | ° / | ° | ° / | | |
| | 170 | 151 15 | N. 61 15 E. | 1 | 15 30 | May 3 | Aug. 11 |
| ne ... | 166 | 147 15 | N. 57 15 E. | ‡ (assumed) | 17 8 | May 9 | Aug. 5 |
| ve..... | ... | ... | ... | ... | 16 19 | May 6 | Aug. 8 |

Table IV.—May-year Alignments in England, for Comparison.

| | Alignment. | Azimuth. | Elevation of horizon. | Declina- tion N. | Dates. | |
|---------|-----------------------------------|-------------|-----------------------------|------------------------|----------|---------|
| | | | | | May. | August. |
| | | ° / | ° / | ° / | | |
| | Circle to two large menhirs | N. 66 50 E. | 1 0 | 14 55 | May 1 | Aug. 13 |
| | Circle to Fougou | N. 64 0 E. | 0 30 | 16 21 | May 6 | Aug. 8 |
| | Circle to Longstone | N. 67 20 E. | 1 18 | 15 3 | May 2 | Aug. 13 |
| | To W. Lanyon Quoit | N. 67 0 E. | 0 0 | 14 3 | April 29 | Aug. 16 |
| | Direction of avenue | N. 67 0 E. | 0 30 (assumed) | 14 23 | April 30 | Aug. 15 |
| | Holy well to Trevethy cromlech | N. 64 0 E. | 0 30 (assumed) | 16 21 | May 6 | Aug. 8 |
| h | Orientation of cromlech ... | N. 64 0 E. | 1 30 | 16 55 | May 8 | Aug. 6 |
| | " " ... | N. 64 0 E. | 1 30 | 16 55 | May 8 | Aug. 6 |
| ve..... | ... | ... | ... | 15 38 | May 4 | Aug. 10 |

In addition to those given in Table IV, I have found* that Lukis† and give plans of a number of cromlechs in Cornwall which appear to be aligned to the May sun.

* See 'Nature,' No. 1987, vol. 77, p. 84, November 28, 1907.

† 'The Prehistoric Stone Monuments of Britain—Cornwall.'

‡ 'Antiquities of Cornwall.'

They are as follows :—

| Cromlech. | Authority. | Azimuth. |
|----------------------------|------------------------|---------------|
| | | . |
| Ianyon Quoit | Borlase; plate xxi ... | N. 66 E. |
| Mulfra Quoit | Lukis; plate xix | N. 63 E. |
| Chywoone Quoit | Lukis; plate xx | N. 64 E. |
| Zennor Quoit | Lukis; plate xxi | N. 64 E. |
| Three Brothers Grugith ... | Lukis; plate xxiii ... | N. 64 E. |
| Mean of above ... | | N. 64° 12' E. |

Assuming an elevation of the horizon between $\frac{1}{2}^{\circ}$ and 1° , this mean value is the exact azimuth of the May sunrise in Cornwall.

Clock-stars.

Table V contains the results for 15 circles, in each of which the observation of a clock-star* appears to be indicated. From the data in the table, the declinations of the stars were determined from a curve connecting azimuth and declination, for different elevations of the horizon, for the general latitude of 57° N.; consequently they are not final, but are sufficiently accurate for a preliminary discussion.

Between 2000 B.C. and 1 B.C. Arcturus and Capella were the only first-magnitude stars to come within the declination range shown in the table, and, as my results show that they were used as clock-stars in Cornwall and Devon,† I consider that the evidence in their favour warrants the assumption that one of them was used as a clock-star by the circle-builders of Aberdeenshire, therefore I give the dates for Arcturus and Capella respectively.

* See 'Roy. Soc. Proc.,' vol. 77, pp. 465—466.

† 'Roy. Soc. Proc.,' *loc. cit.*

Table V.

| Circle at— | Azimuths. | | | Elevation of the horizon. | Declina- tion N. | Dates B.C. | |
|-------------------------|--------------------------------------|--------------------------------|--|---------------------------------|------------------------|------------|----------|
| | Magnetic mean of observations. | True, from N. through E. | True, at right-angles across circle. | | | Arcturus. | Capella. |
| | ° / | ° / | ° / | ° | ° / | | |
| Bracehead Leslie..... | 132 20 | 113 35 | N. 23 35 E. | 1½ | 30 58 | 250 | 2000 |
| Leylodge..... | 123 0 | 104 15 | N. 14 15 E. | 0 | 31 18 | 330 | 1940 |
| Loudon Wood..... | 120 40 | 101 55 | N. 11 55 E. | 0 | 31 38 | 370 | 1890 |
| Connagorn..... | 124 0 | 105 15 | N. 15 15 E. | ½? | 31 42 | 390 | 1860 |
| Wanton Wells..... | 130 30 | 111 45 | N. 21 45 E. | 2 | 31 52 | 420 | 1830 |
| Old Keig..... | 138 0 | 119 15 | N. 29 15 E. | 4 | 31 55 | 430 | 1820 |
| South Fornet..... | 116 48 | 98 3 | N. 8 3 E. | 0 | 32 4 | 450 | 1800 |
| Nether Boddam..... | 130 0 | 111 15 | N. 21 15 E. | 2 | 32 8 | 460 | 1790 |
| Aiky Brae..... | 113 0 | 94 15 | N. 4 15 E. | 0 | 32 18 | 500 | 1760 |
| Castle Fraser..... | 129 36 | 110 51 | N. 20 51 E. | 2½ | 32 43 | 570 | 1680 |
| New Craig..... | 129 34 | 110 49 | N. 20 49 E. | 2½ | 32 43 | 570 | 1680 |
| Loanhead of Daviot ... | 116 45 | 98 0 | N. 8 0 E. | 1 | 33 14 | 660 | 1580 |
| Kirkton of Bourtie..... | 123 30 | 104 45 | N. 14 45 E. | 2½ | 33 57 | 770 | 1460 |
| Lothie Muir..... | 127 40 | 108 55 | N. 18 55 E. | 4 | 34 42 | 920 | 1300 |
| Salie the Greater..... | 113 30 | 94 45 | N. 4 45 E. | 2½ | 35 5 | 980 | 1230 |

Comparing these results with those given for the English circles in the previous paper,* the similarity of the object in view, and the means of attaining it, are, I think, obvious.

The mean date for Arcturus is about 600 B.C., and for Capella about 1600 B.C. Collateral evidence suggests that Arcturus was the clock-star employed, but more observations and enquiries are necessary to determine finally this point.

Due North Alignments.

In addition to the circles mentioned above, there are four in Aberdeenshire in which the alignments are due north. They are respectively situated at Dyce, Whitehill Wood, Raes of Clune and Candle Hill (Insch), and probably represent a later development when the observer's knowledge was so far advanced that he needed only the cardinal point in order to recognise the clock-stars which it was necessary for him to observe.

My best thanks are due to Dr. Angus Fraser, Aberdeen; Mr. Ritchie, Port Elphinstone; Mr. Braid, Durris; Rev. D. Forrest and Mr. Ainslie, Mintlaw; and Colonel Smith and Mr. J. Graham, Callander, Insch, who assisted me in many ways in the different localities. Mr. W. E. Rolston, F.R.A.S., one of my staff, has computed the declinations and assisted in the preparation of this paper; the dates corresponding with the declinations involved have been taken from tables furnished by Mr. J. N. Stockwell, of Cleveland, U.S.A.

* 'Roy. Soc. Proc.,' vol. 77, pp. 467—468, March 19, 1906.

On the Determination of Viscosity at High Temperatures.

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(Communicated by Professor Andrew Gray, F.R.S. Received January 22,—Read
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A large number of viscosity determinations have been carried out with liquids at temperatures near the ordinary room temperature, and some observations at lower and higher temperatures have also been made by similar methods to those adopted for working at the usual temperatures.

Measurements at temperatures higher than 300° to 400° C. present considerable difficulties, and until the present year this subject had not even been touched by experimenters.

As I was anxious to determine the viscosity of substances which melt at temperatures up to a white heat, I lately set myself to work out a satisfactory method of determination.

The present communication contains a description of the method used. The method is suitable for the measurement of the viscosity of liquids which are not very viscous—not more than say 50 times as viscous as water, and is especially designed for the determination of the viscosity of molten metals and salts. The determination of the viscosity of salts up to 1200° C. or even higher, can be quite satisfactorily carried out by this method. Determinations of the viscosity of metals are much more difficult, owing to the impossibility of preventing a certain amount of surface oxidation. The smallest trace of surface oxidation will completely spoil a series of observations, and the prevention of oxidation is really the chief difficulty in such determinations.

Previous Work in this Branch.

The usual method adopted for the determination of viscosity at ordinary temperatures depends on the rate of flow of the liquid through a capillary tube. The determination is easy to carry out, the calculation of the viscosity from the time of flow is simple, and the experimental results are in close agreement with the laws of flow deduced from theoretical considerations.

The glass capillary has been used up to 250° C. by Beck* for the determination of the viscosity of fused mercury salts. With a Jena glass tube the method has been used as high as 600° C. for the determination of

* 'Zeit. für Physikal. Chem.,' 1907, vol. 58, pp. 425—441.

the viscosity of lead salts.* A platinum capillary has been used as high as 500° C. by Goodwin and Mailey.† It is probable that this is about the limit of temperature to which the capillary method may be used, and in any case it did not appear that this method was likely to be employed with good results for metals of even comparatively low melting point.

A rough method of determining the viscosity of molten silicates, depending on the rate at which a platinum wire sinks in the liquid, has been used by Doelter.‡ An advance on this is an interesting apparatus used by Arndt,§ who measured the rate at which a platinum cylinder fell in the liquid. These methods of Doelter and Arndt can only be used for very viscous substances—for liquids whose viscosity is more than 1000 times that of water. They are of no use for measurements on ordinary salts and metals, which appear, in general, to have a viscosity not more than 100 times that of water.

Method.

The method used is based on the method originally given by Coulomb,|| the modifications introduced being due to the special nature of the determinations. In Coulomb's method a horizontal disc is allowed to execute horizontal vibrations about a vertical suspending wire attached to its centre. The viscosity of the liquid can be calculated from the rate of decay of amplitude.

In recent years this method has not been used to any great extent for ordinary viscosity determinations, and this can probably be explained from the following facts:—

(1) The disc used has to be fairly large (15 to 20 cm. diameter is usual), and this involves the use of rather large quantities of liquid; (2) the calculation of viscosity from the observations of experiment is much more involved than in the case of the capillary method; (3) an error made in the observations produces a much greater error in the (calculated) value of the viscosity. While it is not possible to get rid of these last two difficulties, this method is nevertheless capable of giving good results, and the time necessary to carry out a determination is certainly less than that occupied by a determination according to the capillary tube method.

The apparatus as employed by Coulomb consisted of a vertical rigid metal rod several inches in length, which was fixed at its upper end into the centre

* Lorenz and Kalmus, 'Zeit. für Physikal. Chem.,' 1907, vol. 59, pp. 244—251.

† 'Amer. Chem. Soc. Trans.,' 1907, vol. 11, pp. 211—223.

‡ 'Sitz. der Kais. Akad. Wiss. Wien,' 1905, vol. 114, p. 529.

§ 'Zeit. für Elektrochem.,' 1907, vol. 13, pp. 578—582.

|| 'Mem. de l'Institut Nat. des Sciences et Arts,' 1800, vol. 111, p. 246.

of a graduated metal disc, and at its lower end into another disc which was ungraduated. The centre of the upper disc was provided with a small screw arrangement for the reception of the suspension wire, the upper end of which was fixed to a rigid support. The apparatus was first of all made to oscillate in air, and the logarithmic decrement of the amplitude obtained. The lower disc was then submerged in a number of liquids, and the logarithmic decrements noted. After deducting the value for air from that obtained for each liquid, it was possible to compare the viscosities of liquids whose densities were known.

The method has been considerably improved and made much more sensitive by Stokes,* Clerk Maxwell,† and Meyer,‡ and it has been shown that the viscosity (η) of a liquid is given by the equation

$$\lambda - \lambda_0 = C_1 \sqrt{d\eta} + C_2 \eta + C_3 \eta d, \quad (1)$$

where λ and λ_0 are the logarithmic decrements of the apparatus in the liquid and in air, C_1 , C_2 , and C_3 are constants depending on the apparatus, and d is the density of the liquid. This method is found to give results which agree well with theory except in the case of very viscous liquids.

In adapting this method to high temperature work the following difficulties have to be encountered:—

(1) It is not practicable, when working on a laboratory scale, to keep large quantities of liquid at a high temperature; it is desirable, therefore, to make the method work with an amount of liquid which will be taken by a crucible, say 3 inches deep and $2\frac{1}{2}$ inches in diameter. The dimensions of the immersed solid must therefore be small.

(2) The solid whose oscillations are to be damped, and other accompanying parts, cannot be made too small, as the sensibility of the apparatus is thereby decreased, and also as the molten salts or metals corrode the parts immersed too rapidly.

(3) The liquids, especially the metals, have a comparatively high density and the apparatus must be made to sink in these to the proper depth.

A consideration of the decay of amplitude in torsional oscillation, when applied to viscosity determinations, shows that it is made up of three parts: the first due to the defective elasticity of the wire, the second to the viscosity of the liquid, and the third due to the loss of energy consequent on a simple movement of translation being imparted to the liquid. If

* 'Camb. Phil. Soc. Trans.,' 1850, vol. 9, II, p. 8.

† 'Phil. Trans.,' 1868, vol. 156, pp. 249—268.

‡ 'Pogg. Ann.,' 1865, vol. 125, p. 177.

represent the amplitude and t the time, the decrease in amplitude from these causes is given as follows:—

$$-\frac{dA}{dt} = k_1 A, \quad -\frac{dA}{dt} = k_2 A, \quad -\frac{dA}{dt} = k_3 A^2,$$

where k_1 , k_2 , and k_3 are constants.

Combining these we have

$$-\frac{dA}{dt} = (k_1 + k_2) A + k_3 A^2. \quad (2)$$

If A is small, and if k_3 is small, i.e., if the translation movement communicated to the liquid is small,

$$-\frac{dA}{dt} = (k_1 + k_2) A,$$

or

$$k_1 + k_2 = \frac{1}{t} \log \frac{A_0}{A_t}, \quad (3)$$

where A_0 and A_t are the values of A at the beginning and after time t . In this case the logarithmic decrement for successive oscillations is constant.

If the velocity of movement of the liquid is considerable, the last term cannot be neglected and the integral has the form

$$k_1 + k_2 = \frac{1}{t} \log \frac{A_0}{A_t} - \frac{1}{t} \log \frac{k_1 + k_2 + k_3 A_0}{k_1 + k_2 + k_3 A_t}. \quad (4)$$

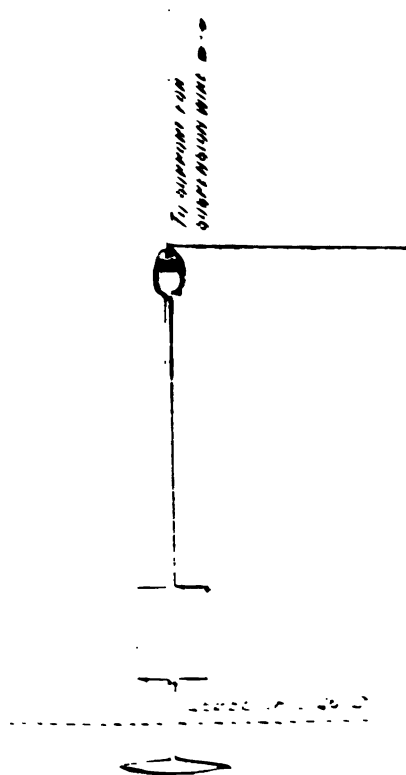
In this case the logarithmic decrement is not constant for any one series of observations, but varies with the amplitude. As it is necessary that the oscillations should conform to equation (3), the energy of motion communicated to the liquid has to be kept to a minimum. It follows that the body submerged must be of such a form that a horizontal section through any point will be circular. A circular disc, a sphere or a cylinder are all quite suitable, but after some trials with these I have returned to the disc, finding it best suited to the present purpose. The disc used was 26 mm. in diameter and 1 to 3 mm. thick. For temperatures up to 400° C. the diameter of the stem (which forms the axis of rotation) was 1 to 3 mm.; for higher temperatures it was 3½ to 5½ mm. It is very important that the disc should be an exact circle, and should rotate truly about its axis. It is not possible to obtain for the manufacture of the disc any material which is heavy enough to sink in metals, and at the same time resistant enough to stand the corrosion and heat of the liquid in which it is placed. The only way out of this difficulty seemed to be to weight the apparatus externally. The amount of this weight and its distance from the disc must be such as to keep the centre of gravity of the rigid part of the apparatus as low as possible, otherwise the apparatus will not swing evenly and the path of

any particle of the disc becomes an ellipse instead of a circle, thus making the motion correspond to equation (4) instead of to equation (3). The weight used was a small iron cylinder clamped on to the stem about $1\frac{1}{2}$ to 2 inches above the disc. For temperatures up to 400° C. iron is quite suitable as a material for the disc. For temperatures up to a white heat one may use either fireclay, or a mixture of fireclay and plumbago. In making a series of observations with this apparatus, the disc is allowed to sink about half an inch below the surface of the liquid. The amplitude of the oscillations is indicated by a pointer (wire) at right angles to the top of the iron rod which carries the disc, and the pointer moves above a circular scale divided into degrees. The accuracy of the observation is not greater than $\frac{1}{4}^{\circ}$ to $\frac{1}{2}^{\circ}$,

and the average value of the logarithmic decrement as obtained from a series of observations is accurate to about 2 per cent. The readings could be made more accurate than this if some other method of recording were adopted, but a series of trials in high temperature work have shown that errors from other sources are much too great to make any further refinement of this kind necessary. With this apparatus, the determination of the viscosity of a liquid is accurate to within 5 per cent. of the absolute value, unless there are special circumstances, as in the case of molten metals, when the results are apt to come out considerably too high.

The apparatus used in my determinations is shown in the accompanying figure. The length and the diameter of the suspending wire are regulated by the period which it is desired to give the apparatus. The period in my ex-

periments varied between 17 and 1 seconds. The period of the oscillations in the liquids used hardly varied at all. The period in the case of mercury was only 10 per cent. greater than in the case of water.



The Calculation of the Viscosity from an Experimental Determination of the Logarithmic Decrement.

In obtaining the logarithmic decrement, Briggs' logarithms have been used throughout.

The constants C_1 , C_2 , and C_3 in equation (1) are best determined empirically from determinations on three liquids of known viscosity and density. Knowing C_1 , C_2 , and C_3 , the viscosity of any other liquid can be determined by solving the quadratic equation

$$(C_2 + C_3d)S^2 + C_1\sqrt{d}S - (\lambda - \lambda_0) = 0,$$

where

$$S = \sqrt{\eta}.$$

The expansion of the disc at high temperatures is very small, but a slight correction has to be made on account of the slightly larger surface in contact with the liquid. If r be the radius of the disc, the surface in contact with the liquid is approximately equal to $2\pi r^2$.

The coefficient of expansion for the surface is equal to twice the coefficient of linear expansion for the material composing the disc. The coefficient of linear expansion for iron is 0.00001, and for fireclay it is probably about 0.000005. Each unit of surface will therefore increase by 0.00002 per degree in the one case and 0.00001 in the other. The logarithmic decrement is proportional to the surface in contact with the liquid, and a slight correction must therefore be made on this according to the temperature of experiment.

Experimental.

There has occasionally existed in the minds of previous workers with the scillation method some doubt as to whether this was a real test of the internal friction of the liquid. If any slipping takes place at the surface of contact between the solid and the liquid, the method is really of very little use. This point was therefore tested first of all. The experiments show that slipping does not take place to any detectable extent; this holds good even for liquids like mercury, which do not "wet" the solid. We can therefore assume that the layer of liquid next the solid moves with the same velocity as the solid itself. If any slipping took place the amount of slip would be different for different liquids and for different solid surfaces. A number of different discs gave the following results:—

Table I.

| Material of disc. | Diameter of disc. | Thick-ness of disc. | Value of logarithmic decrement. | | | | |
|-----------------------------------|-------------------|---------------------|---------------------------------|-----------------|-----------------------|-------------------|-------------------|
| | | | Air. | Water (20° C.). | Chloro-form (20° C.). | Mercury (20° C.). | Alcohol (20° C.). |
| 1. Iron with smooth surface | mm. 26 | mm. 0·85 | 0·0097 | 0·0294 | 0·0285 | 0·0889 | 0·0293 |
| 2. " rough " | 26 | 0·85 | 0·0097 | 0·0297 | 0·0275 | 0·0900 | 0·0293 |
| 3. Glass with rough surface | 26 | 0·85 | 0·0097 | 0·0298 | 0·0273 | 0·0908 | — |
| 4. " smooth " | 26 | 1·12 | 0·0097 | 0·0318 | 0·0301 | 0·1031 | — |

Any differences in the results of Cases 1, 2, and 3 may be put down to experimental error. The somewhat higher figures obtained in the fourth case are due to the disc being thicker; it will be noticed that the proportionate increase is practically the same for all the liquids. It is assumed from these results that there is no slipping at the surface of contact.

The method was next tested with liquids of known viscosity. Taking three of these as standards the viscosity of the others was calculated. The results are given in the next table.

The values of density and viscosity in the table are taken from Landolt and Bornstein's tables with the exception of some density values obtained from the researches of Patterson.*

Table II.—Iron Disc 26 mm. diameter. Period of oscillation, 7·5 seconds.

| Substance. | Temperature. | Logarithmic decrement. | The same minus value for air. | Density. | Absolute viscosity (known)- |
|---------------------|--------------|------------------------|-------------------------------|----------|-----------------------------|
| | ° C. | | | | |
| Air | 20 | 0·0105 | — | — | — |
| Water | 20 | 0·0557 | 0·0452 | 0·998 | 0·0102 |
| Chloroform | 20 | 0·0468 | 0·0363 | 1·49 | 0·00565 |
| Mercury | 20 | 0·1760 | 0·1655 | 13·55 | 0·0169 |
| Benzene | 20 | 0·0427 | 0·0322 | 0·879 | 0·0066 |
| Ethyl alcohol | 20 | 0·0575 | 0·0470 | 0·791 | 0·0119 |

Using water, chloroform, and mercury to calculate the constants from, have

$$C_1 = 0·3148, \quad C_2 = 1·3232, \quad C_3 = -0·00753.$$

We may now use these values to calculate the viscosity of benzene and alcohol from the observed logarithmic decrements. The values obtained are

* 'Journal Chem. Soc.,' for the last few years.

0.00645 and 0.0121 respectively, which compare well with the values given in Table II. The same apparatus gave the following results for mercury at high temperatures :—

Table III.—Mercury at High Temperatures.

| Temperature. | Logarithmic decrement. | Logarithmic decrement minus the value for air and corrected for expansion. | Density. | Absolute viscosity according to Koch.* | Absolute viscosity calculated from logarithmic decrement. |
|--------------|------------------------|--|----------|--|---|
| ° C. | | | | | |
| 65 | 0.1632 | 0.1526 | 13.43 | 0.0136 | 0.0138 |
| 95 | 0.1638 | 0.1431 | 13.39 | 0.0125 | 0.0124 |
| 133 | 0.1481 | 0.1373 | 13.27 | 0.0114 | 0.0116 |
| 216 | 0.1413 | 0.1302 | 13.08 | 0.0100 | 0.0106 |

* 'Ann. der Physik,' 1881, vol. 14, pp. 1—12.

An example of a determination of viscosity at a somewhat higher temperature is given in Table IV. The values of the density and viscosity for sodium nitrate have already been determined by the capillary method.* These values are given in the table along with the values of viscosity calculated from the logarithmic decrements using the same density values. The disc used was one of fireclay, 27 mm. in diameter. The constants C_1 , C_2 , and C_3 , as determined by oscillations in water, mercury, and chloroform, were

$$C_1 = 0.4595, \quad C_2 = 1.238, \quad C_3 = -0.2052.$$

Table IV.—Sodium Nitrate (Melting Point 309° C.).

| Temperature. | Logarithmic decrement. | The same minus value for air. | The same corrected for expansion. | Density (Goodwin and Mailey). | Viscosity (Goodwin and Mailey). | Viscosity (from logarithmic decrement). |
|--------------|------------------------|-------------------------------|-----------------------------------|-------------------------------|---------------------------------|---|
| ° C. | | | | | | |
| 320 | 0.1440 | 0.1335 | 0.1337 | 1.91 | 0.0282 | 0.0291 |
| 368 | 0.1255 | 0.1150 | 0.1146 | 1.89 | 0.0227 | 0.0228 |
| 390 | 0.1180 | 0.1075 | 0.1071 | 1.86 | 0.0191 | 0.0205 |
| 435 | 0.1053 | 0.0948 | 0.0944 | 1.83 | 0.0160 | 0.0165 |
| 450 | 0.1022 | 0.0917 | 0.0914 | 1.82 | 0.0152 | 0.0156 |

The numbers in the last two columns agree within the experimental error. These results show the availability of this method for the determination

* Goodwin and Mailey, *loc. cit.*

of viscosity up to the highest temperature at which a platinum capillary has been used. As the fireclay or graphite disc remains uncorroded at temperatures of 1000° C. and over, the method is quite well suited for high temperature work. I am now engaged on viscosity measurements with a number of salts and metals, and hope before long to report on these.

Any expenses connected with this investigation have been defrayed by grants from the Chemical Society and from the Carnegie Trust for the Universities of Scotland.

BAKERIAN LECTURE for 1907.—*On the Atomic Weight of Radium.*

By T. E. THORPE, C.B., LL.D., F.R.S.

(Delivered June 20, 1907 ; MS. received in completed form, March 5, 1908.)

Although there has been a considerable amount of discussion, based upon spectroscopic considerations and on its supposed mode of genesis, respecting the place of radium in the system of the elements, and inferentially, therefore, concerning its atomic weight, we are indebted for the only direct experimental determinations of this value hitherto made known to the discoverer of the element, Mme. Curie. Her first observations, published in 1902, were made on about 90 milligrammes of the chloride, and furnished the value 225 as the mean of three fairly concordant experiments.*

In the autumn of last year Mme. Curie communicated to the French Academy the results of a second series of estimations. These were made upon much larger quantities of the carefully purified chloride (about 4 decigrammes) and afforded the value 226.2 as the mean of three closely concordant determinations ($\text{Ag}=107.8$, $\text{Cl}=35.4$).†

In 1906, at the instance of Sir William Huggins, then President of the Society, and by the aid of the kind interest shown by H.R.H. the Prince of Wales, the Austrian Government placed about 500 kilogrammes of pitchblende residues from the mine at Joachimsthal at the disposal of the Royal Society. These residues were sent to be worked up by M. Armet de Lisle at his factory at Nogent-sur-Marne, by the method employed by him in the case of the

* 'Ann. de Chim. et de Phys.,' vol. 30, 1903.

† 'Comptes Rendus,' 1907, vol. 145, p. 422 ; 'Le Radium,' October, 1907.

material which served M. and Mme. Curie for their researches. The funds for both these purposes were defrayed from a grant made by the Goldsmiths' Company to the Royal Society in 1904 for the purpose of the investigation of radium.

The residues, as received by M. Armet de Lisle, were stated to have a radio-activity of about $2\frac{1}{2}$ times that of uranium.

The process of extraction employed by M. Armet de Lisle resulted in the production of about 413 grammes of practically anhydrous barium chloride, containing radium chloride sufficient to give the salt a radio-activity 560 times that of uranium.

This salt was received by the Royal Society in the autumn of 1906, and was handed to me in January, 1907, with the request that I would extract the radium chloride from it, and undertake, if possible, a redetermination of the atomic weight of the element. This in view of the discussion, already referred to, which was then taking place as to the relation of radium to certain other elements, seemed at the time the most profitable use to which the radium salt, when extracted, could be put. When received by me the barium-radium chloride was distinctly cream-coloured, and the bottle in which it was contained was coloured violet.

The method of extraction was substantially the same as that originally adopted by Mme. Curie, and described in her thesis,* namely, systematic fractional crystallisation, first from water and then from increasingly strong hydrochloric acid, until finally the acid used was the strongest that could be obtained by distillation. All the solvents employed were carefully purified, the acid being distilled in a platinum retort, and preserved in a platinum bottle. The crystallisations were made first in porcelain, subsequently in Jena glass, and finally, as the radio-active matter became more and more concentrated, in vessels of fused rock-crystal. Every precaution was taken to guard against loss and accidents, and to ensure the recovery of the radium should such occur. It is satisfactory to be able to state that the whole scheme of extraction, involving some 9400 recrystallisations, was carried through without a mishap.

I have to thank Mme. Curie for her courtesy in affording me information concerning certain details of her method of isolating the radium salt. At the outset of our exchange of letters she informed me, of what at the time I was unaware, that she was then actually engaged on the same problem, and she has since, as already stated, published the results of her determinations. She was good enough, however, to express the hope that I would continue the work which I had been requested to undertake, in view of the desirability

* *Loc. cit.*

of gaining all possible knowledge as to the true atomic weight of the element.

During the autumn of 1907, whilst still engaged in the isolation of the radium chloride from the material furnished by M. Armet de Lisle, I received a further small supply of radium from the Royal Society. It was bought in Cambridge and was of German origin, and had been purchased through the instrumentality of Professor Liveing. It purported to be radium bromide, but on removing it from the metallic capsule in which it had been stored since 1903, it was found to be wholly insoluble in water. On treatment with pure dilute hydrobromic acid it readily passed into solution. The salt obtained by evaporation was sent to Professor Rutherford, who had kindly undertaken to make any measurements of radio-activity which I needed. He estimated the amount of radium present as equivalent to 33 milligrammes of radium bromide.

This salt was eventually converted into chloride, and was purified by repeated crystallisation from strong hydrochloric acid.

Traces of lead cling persistently to the radium chloride thus separated by means of hydrochloric acid. Mme. Curie was so kind as to draw my special attention to this fact, and accordingly care was taken to remove this metal. When practically the whole of the radio-active matter had been concentrated into a few grammes of the material, this was dissolved in water acidulated with hydrochloric acid, and treated with sulphuretted hydrogen out of contact with air. A small precipitate of lead sulphide was formed. The liquid was further treated with sulphuretted hydrogen, the lead sulphide removed by filtration, the filtrate evaporated to dryness, the residue treated with strong hydrochloric acid, and the process of fractionation resumed. That the precipitate was lead sulphide was confirmed by its conversion into the yellow iodide. •

Determination of Atomic Weight.

This was effected by ascertaining the amount of silver chloride yielded by a weighed quantity of the anhydrous radium chloride—the principle of the method already employed by Mme. Curie.

Since it was very improbable that the amount of the radium salt at my disposal would amount to as much as a decigramme, it was absolutely necessary so to arrange the process of carrying out the estimations as to minimise, to the greatest possible extent, the errors due to manipulation. Accordingly a method was devised whereby the whole of the operations of drying and weighing the radium chloride, precipitating, washing, drying and weighing the silver chloride, might be performed in one and the same vessel, thus

bviating the necessity of transferring the silver salt, and of separating it by any of the ordinary processes of filtration.

The vessel in which these operations were made consisted of a thin glass tube with a conical base furnished with a hollow well-ground stopper. It had a capacity of about 15 c.c., and was as light as was consistent with the requisite strength, and could be suspended from the balance-arm by fine platinum wire. In all the weighings a precisely similar bottle of almost identical weight and capacity, suspended in like manner, was employed as a tare. The weighings were made on a very sensitive assay balance, with 10-inch arms, carrying a maximum load of 12 grammes and provided with eight stirrup pans. I am indebted to Mr. Oertling for the loan of it. It was a beautifully finished instrument of great delicacy, and remarkably constant in its indications (fig. 1).

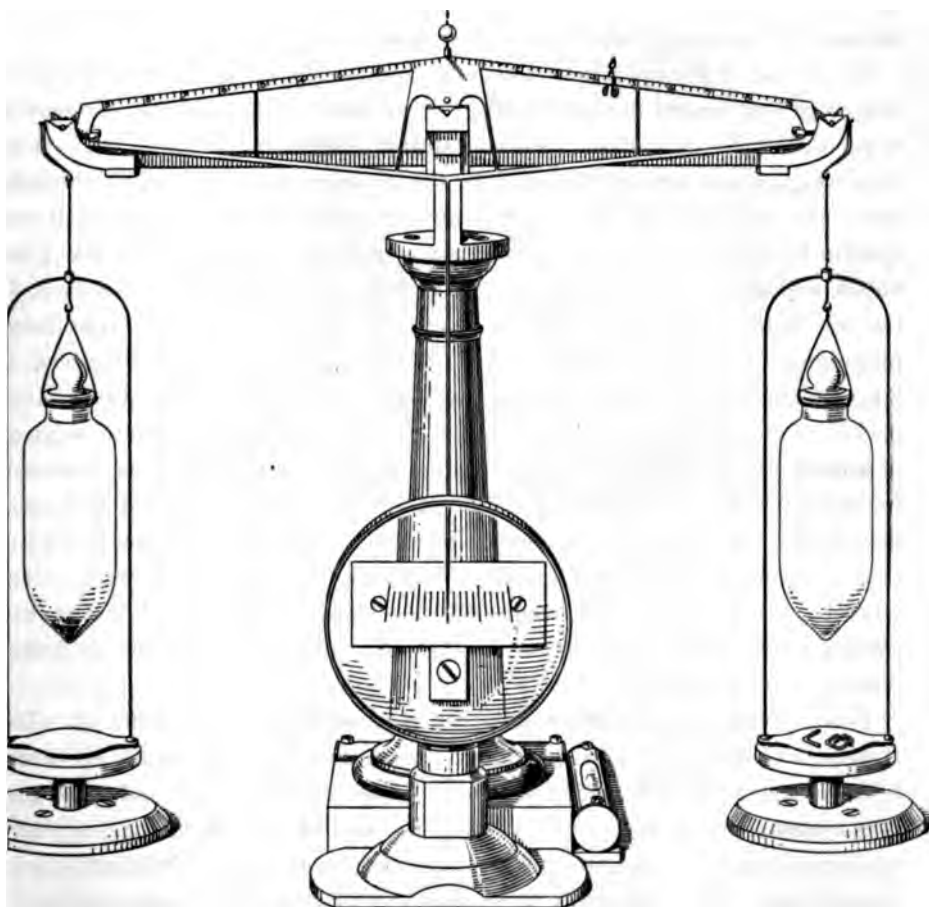


FIG. 1.

The weights were also of Oertling's make, and were compared before use with a standard set belonging to the Government Laboratory.

A room was specially set apart and arranged for the determinative work. It was a small apartment on one of the upper floors of the Government Laboratory and had a wooden block floor arranged "herring-bone" fashion. The walls of the building were subject to a very slight tremor, due to a small steam engine in the basement. The balance table, therefore, was not belted to the walls, as is the usual practice, but was placed directly on the floor, which, by reason of its mode of construction, was less susceptible to tremor than the walls. The legs of the table stood on packets of filter paper, as did also the levelling screws of the balance case. Under these conditions the balance was found to be quite free from tremor and the levels remained absolutely constant throughout the entire course of the work.

The weighings were made by the method of vibrations, the zero-point being determined before and after each determination.

The course of the operations was as follows:—The small glass vessel and its tare were first heated to about 150° in an air bath for an hour and allowed to stand overnight in a desiccator containing phosphoric oxide. They were then weighed one against the other in the manner described. The chloride, previously dried at 140° to 150° , was next transferred by means of a platinum spatula from the rock-crystal basin in which it was contained, to the glass vessel, and this and its tare were again heated to 150° for about an hour in the air bath, and, after standing overnight in the desiccator containing phosphoric oxide, were again weighed. The chloride was then dissolved in 2 c.c. of distilled water, the solution acidulated with two drops of dilute nitric acid (1:4), warmed and mixed with a slight excess of silver nitrate solution of known strength added drop by drop, with constant shaking, from a narrow burette capable of being read to $1/50$ c.c. When clear, the liquid was again tested with the silver nitrate solution in order to ascertain that the precipitation was complete, and after standing for about 18 hours in a warm place when the silver chloride had wholly subsided into the bottom of the conical portion of the vessel, the clear supernatant solution was drawn off by means of a capillary glass tube.

This was conveniently effected in the manner illustrated by fig. 2. The vessel (*a*) containing the silver chloride was placed on the small elevating table (*b*), the height of which could be adjusted by means of the rack and pinion arrangement seen at (*c*), so that the end of the drawn out capillary syphon (*d*), made of thermometer tubing, could be brought to within a millimetre or two of the deposit of silver chloride. By gentle aspiration at (*e*) the action of the syphon was started, and by far the greater quantity of the clear

liquid could be drawn over into the flask (f) without the slightest risk of disturbing the precipitate.

The table was then lowered, and the end of the syphon as well as the internal sides of the vessel washed by a fine stream of hot distilled water. After clarification, the wash-water, which was about 4 or 5 c.c. in bulk, was drawn over as before, and the process repeated. After each addition of hot water the vessel containing the silver chloride was well shaken, and the

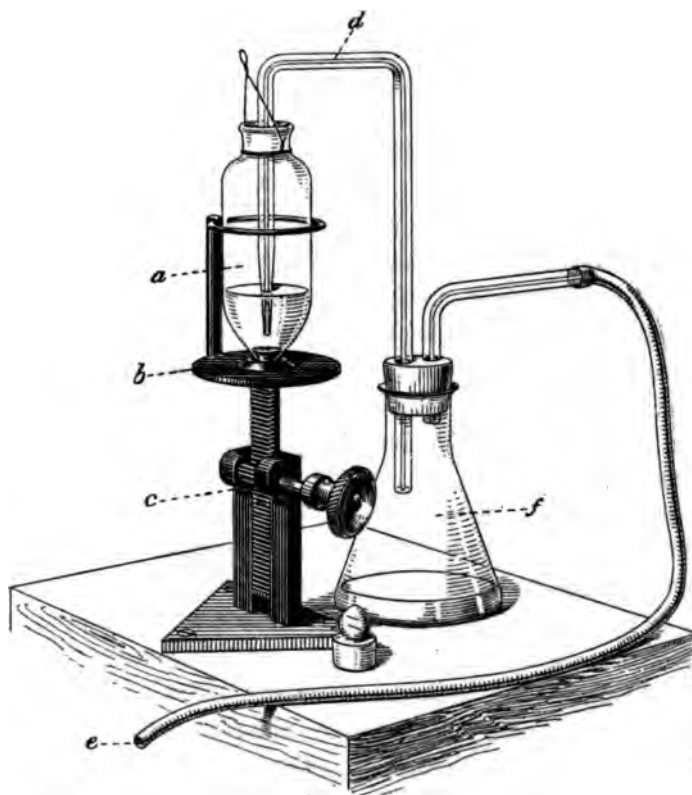


FIG. 2.

precipitate broken up by means of a fine platinum wire, so as to bring the washing water in thorough contact with it. As is well known, silver chloride which has become granular by standing shows little or no tendency to occlude soluble matter and is readily washed. Both the end of the syphon and the platinum wire were always washed by a stream of hot water and were carefully examined by a lens, but in no case was any silver chloride found to have become attached. The liquid drawn over was invariably perfectly clear.

Assuming that we have 100 milligrammes of soluble matter in the 4 c.c. of the clear supernatant liquid and that we draw over 3.5 c.c. at each successive

operation as above described, it is readily calculable that the amount of matter in solution, even after the third operation, is probably too small to be appreciated by the balance.

The following table shows how rapidly the soluble matter is removed by systematic washing in the manner described.

| | Milligrammes. |
|--|---------------|
| Original solution contains | 100 |
| After first decantation, residual liquid | 12.5 |
| „ first washing „ „ | 1.56 |
| „ second „ „ „ | 0.19 |
| „ third „ „ „ | 0.02 |
| „ fourth „ „ „ | 0.003 |
| „ fifth „ „ „ | 0.0004 |

As the precipitated silver haloid was always thus washed six times in succession, it may be assumed that it was practically freed from all soluble matter.

Care was of course taken to protect the silver chloride from the action of light, and to the extent that was practicable all the operations were carried out in a photographic dark room which adjoined the small laboratory set aside for the work. No matter what precautions were taken to exclude ordinary white light, the silver chloride invariably became violet in contact with radium solutions.

The washed silver chloride was first dried at 100° and then heated in the air bath to 160° for about a couple of hours, and, after standing in the desiccator over phosphoric oxide for about 18 hours, weighed in the manner described.

In order to test the practicability of the method and to acquire experience of its working, as well as to gain some idea of its accuracy before actually making use of it in the case of the radium salt, a series of determinations of atomic weight was made with barium chloride, purified by systematic recrystallisation from water, according to the method already indicated, the same apparatus, reagents, and solutions being employed as were to be used subsequently in the radium determinations.

The results were as follows:—

$$\text{Ag} = 107.93. \quad \text{Cl} = 35.45.$$

| Barium chloride. milligrammes. | Silver chloride. milligrammes. | Atomic weight, Ba. |
|-----------------------------------|-----------------------------------|--------------------|
| 114.7 | 157.8 | 137.5 |
| 172.1 | 236.8 | 137.5 |
| 57.1 | 78.8 | 136.9 |
| 62.6 | 86.1 | 137.6 |
| 68.1 | 93.7 | 137.5 |

As the corrections for displaced air for the silver chloride and for the barium chloride only amount to 0·00007 and 0·0002 per gramme respectively, they are of course wholly negligible in the case of quantities so small as were actually employed. The value for barium adopted by the International Committee on Atomic Weights, 1907—08, is 137·4.

These determinations were made on independent amounts of material. As the quantity of radium salt I could hope to obtain would almost certainly not suffice to enable me to make similar independent determinations, it was desirable to prove that the element, which would exist in the solution in association with nitric acid after the precipitation of the chlorine as silver chloride, could be recovered and reconverted into chloride; and that the operations necessary to effect this would not influence the value of the atomic weight in a subsequent determination.

The first step was to remove the excess of silver in solution. This might be effected by means of hydrochloric acid. A difficulty at once presented itself. Silver chloride is not wholly insoluble in solutions of hydrochloric acid and of the chlorides of the alkaline earths, and presumably, therefore, in solutions of radium chloride. It was consequently necessary so to apportion the hydrochloric acid as to effect the precipitation of the silver without leaving any considerable excess of hydrochloric acid in solution. As the amount of the silver originally used, as well as that in the weighed silver chloride, were known, it was easy to calculate the amount remaining in solution and so determine the quantity of hydrochloric acid required to precipitate it. This amount of hydrochloric acid, contained in a dilute solution of known strength, was then cautiously added, drop by drop, with constant shaking, and when the liquid was sufficiently clear it was tested, to ascertain that the precipitation was complete, by the addition of a single drop of the hydrochloric acid solution.

After standing until perfectly clear, the supernatant liquid was drawn off by the capillary syphon, the silver chloride thoroughly washed in the manner already described, and the solution transferred to a silica basin and evaporated to dryness over a water-bath heated with an alcohol lamp to avoid any possible action of the oxides of sulphur produced by the combustion of London coal-gas.

The dried residue was then repeatedly evaporated with small quantities of pure hydrochloric acid and so reconverted into the chloride.

Two determinations of the atomic weight of barium, made in the manner described on barium chloride thus recovered, gave the following results:—

| Barium chloride. milligrammes. | Silver chloride. milligrammes. | Atomic weight, Ba. |
|-----------------------------------|-----------------------------------|--------------------|
| 139·5 | 191·4 | 138·1 |
| 78·8 | 108·3 | 137·7 |

In the hope that I might be able to employ the bromide of radium in the determination of the atomic weight of this element, I also made a similar preliminary series of determinations of the atomic weight of barium by means of barium bromide prepared from the pure chloride, and repeatedly recrystallised from alcohol.

The results were as follows :—

$$\text{Ag} = 107\cdot93. \quad \text{Br} = 79\cdot96.$$

| Barium bromide. milligrammes. | Silver bromide. milligrammes. | Atomic weight, Ba. |
|----------------------------------|----------------------------------|--------------------|
| 89·9 | 113·6 | 137·5 |
| 96·0 | 121·4 | 137·3 |
| 111·0 | 140·3 | 137·4 |

Two determinations were made on the recovered barium bromide, with the following results :—

| Barium bromide. milligrammes. | Silver bromide. milligrammes. | Atomic weight, Ba. |
|----------------------------------|----------------------------------|--------------------|
| 91·0 | 114·9 | 137·7 |
| 80·8 | 102·1 | 137·5 |

It will be seen from these numbers that a very close approximation to the true atomic weight of barium can be obtained by the method described, the maximum error being about half a unit, or less than 0·5 per cent. Considering that the atomic weight of radium is probably nearly double that of barium, the same fortuitous errors would affect its value to about a unit.

There is, however, one circumstance which, whilst not without influence in raising the value of barium, when determined on the recovered chloride, hardly affects the value of radium. In the case of radium, the effect of any minute quantity of retained silver haloid in the recovered salt, provided it is weighed with the precipitated silver chloride, is practically negligible, since radium chloride gives approximately its own weight of silver chloride.

As the work of isolating and purifying the radium chloride proceeded, determinations of the amount of chlorine were made as described from time to time, and as soon as approximately constant values were obtained it was assumed that any barium or other impurity present was too small

in amount to affect the results when regard was had to the unavoidable experimental errors. The resulting chloride was then repeatedly and carefully recrystallised from pure, strong, hydrochloric acid, the "tails," which were comparatively rich in radium, being specially set apart.

The purified salt finally extracted from the material supplied by M. Armet de Lisle weighed, when anhydrous, 64 milligrammes.

I regard this salt as substantially radium chloride. I am not, however, in a position to say that it was absolutely free from barium. At the same time, I have reason to believe that the amount still present was probably too small to materially influence the result, considering the limited quantity of the salt I had to work with, and the consequent relatively large experimental errors.

With the aid of Sir William Huggins, who kindly made the spectroscopic trials for me, I was able to carry out Mme. Curie's test of comparing the relative intensity of the lines of barium and radium in the spark spectrum of the separated radium chloride. Mme. Curie compared the relative strengths of lines 4554.2 of Ba and 4533.3 of Rd. Although these have the advantage of being close together, they are of dissimilar intensity. Sir William Huggins advised that a more stringent test would be to take the line 5536.2 of Ba of intensity 10, and compare it with the Rd lines 5813.8 and 5560.8, which are also of intensity 10. On actually making the trials, which were repeated several times, the green Ba line 5536.2, although visible, was seen to be relatively very feeble—less intense, indeed, than that afforded by the most dilute solution of barium chloride that we were able to employ.

With this material, therefore, I attempted to make the determination of atomic weight. Accordingly, the greater portion was transferred to the vessel already described, and the amount of chlorine in the anhydrous salt determined with all possible care. The result was:—

| | | |
|------------------|------------------|--------------------|
| Radium chloride. | Silver chloride. | |
| milligrammes. | milligrammes. | Atomic weight, Rd. |
| 62.7 | 60.4 | 226.8 |

The radium was recovered from the solution, reconverted into chloride, added to what remained of the original quantity, and the amount of chlorine again determined in the anhydrous salt. The second result was:—

| | | |
|------------------|------------------|--------------------|
| Radium chloride. | Silver chloride. | |
| milligrammes. | milligrammes. | Atomic weight, Rd. |
| 63.9 | 61.8 | 225.7 |

The purified chloride obtained from the Cambridge material amounted to

24 milligrammes. A chlorine determination on a portion gave a number exceeding 230 for the atomic weight. No more importance can be attached to this value, considering the very small amount employed, than as showing that the salt was of the same order of purity as that obtained from the French material.

It was accordingly added to the main bulk, and the whole was repeatedly crystallised from strong hydrochloric acid, about 6 milligrammes being thus removed in the mother liquors. The resulting chloride, after being dried at 150° , was again analysed, with the following results:—

| Radium chloride. milligrammes. | Silver chloride. milligrammes. | Atomic weight, Rd. |
|-----------------------------------|-----------------------------------|--------------------|
| 78.4 | 75.3 | 227.7 |

The mean value is 226.7, or, to the nearest unit, 227. This, it will be observed, is in very close accord with Mme. Curie's latest number.

I think, therefore, it is reasonably well established that the atomic weight of radium is now known to within a unit which, considering the relatively high number, is, under the present circumstances, as fair a degree of exactitude as could be anticipated.

There are, however, one or two facts connected with the behaviour of radium chloride which, as they may possibly affect the determination of its atomic weight, may here be mentioned. If a quantity of the salt be kept in perfectly dry air, it will be noticed that it very slowly increases in weight. The increase is very small, but it is plainly perceptible on a sufficiently delicate balance, and in the course of three or four days may amount to 0.3 per cent. On opening the vessel a marked smell of ozone is perceived, and on aspirating the air from above the chloride by means of a capillary tube passing into a freshly-prepared solution of potassium iodide and starch, iodine is found to be liberated, as seen from its action on the starch. Moreover, on dissolving radium chloride which has stood for some time in contact with the air in warm water, and acidulating the solution with dilute nitric acid, a smell recalling that of hypochlorous acid is perceived. The observed increase in weight may be due, therefore, to a portion of the air in the vessel becoming ozonised, or to a slight oxidation of the chloride, or to both these causes combined. Their joint effect would tend to increase the atomic weight of radium.

Another remarkable circumstance connected with radium chloride is its action on colourless rock-crystal, which is gradually turned a deep purplish black. Berthelot has already drawn attention to the action of radium on quartz. The silica vessels which I employed in connection with the foregoing work were thus strongly coloured in the course of a few months.

Moreover, these vessels, as well as those of porcelain and glass, are slightly attacked by radium chloride, with the formation, apparently, of insoluble silicates. A similar observation has been made by Mme. Curie. It occasionally happened that a sample of radium chloride, after standing for some considerable time in contact with glass, gave a faintly turbid solution, although when the salt was newly crystallised from hydrochloric acid its aqueous solution was perfectly clear.

I had hoped, as stated, to have obtained an additional series of values for the atomic weight of radium by the analysis of the bromide. As already mentioned, I reconverted the Cambridge material into this salt; but my experience with it leads me to infer that it is not sufficiently stable to afford trustworthy values for the atomic weight of the element. It appears to lose bromine and eventually becomes insoluble in water. I hope to be able to study this change more minutely, as well as to throw some additional light on the action of radium salts on glass.

In conclusion, I desire to acknowledge my indebtedness to my assistant, Mr. Arthur G. Francis, B.Sc., for the assiduity, conscientiousness, and skill with which he has carried through what has proved to be the most irksome and tedious part of the work, namely, the isolation and purification of the radium chloride.

I am also indebted to Professor Rutherford for the measurements of radio-activity which he made for me in the course of the fractionation of my material.

Alternate Current Measurement.

By W. E. SUMPNER, D.Sc., M.I.E.E.

(Communicated by Professor J. Perry, F.R.S. Received October 5, 1907,—Received January 16, 1908,—Received in revised form January 21, 1908.)

| | |
|--|------|
| Part I.—The Mathematical Relationships of Cyclic Quantities | 311. |
| „ II.—The Action of a Cyclic Magnetic Field on a Movable Coil conveying a Current of the same Frequency | 315 |
| „ III.—The Theory of Shunt Magnet Instruments | 320 |
| „ IV.—Experimental Verification | 327 |

The lack of precision of measurements with alternate currents, as compared with those using direct currents, is mainly due to the relative sensitiveness of the instruments available for such tests. The fact that the turning moment acting on the moving system depends in one case on the square of the current and in the other on the first power of the current, readily explains the high ratio between the currents needed to cause the minimum measurable deflection in the two cases, but this ratio is, nevertheless, most striking when a numerical comparison is actually made on some fair basis. The only likely way at present of improving alternate current instruments is to use iron cored electromagnets to increase the strength of the magnetic field. I have found that the difficulties due to varying permeability and hysteresis of the iron can be avoided by exciting the electromagnet in shunt. It proves possible, with careful design, to construct an electromagnet whose flux is connected with the exciting voltage by a strict mathematical law involving no variable physical properties like permeability, etc. Such an electromagnet is eminently suited for measuring purposes. The theoretical and experimental study of instruments constructed on this principle has brought out certain novel points which are set forth in the present paper.

The first part discusses the mathematical relations of cyclic quantities having a common fundamental period, and constitutes a development of a method already published.* This method is the only one known to me which is independent of assumptions in regard to the wave form of the quantities dealt with. The usual methods, which are based on the erroneous assumptions of sine law wave form, are not any simpler in working, and are most unsatisfactory when the accuracy of new results has to be critically examined. All alternate current measurements refer to mean squares or to mean products, and the natural method of obtaining the connections between

* 'Roy. Soc. Proc.,' vol. 61, 1897.

such squares and products is to study the properties of quadratic functions of the variables. The earliest instance of this in alternate current theory was in connection with the "three voltmeter method."* Such processes lead to a very simple form of calculus appropriate to cyclic quantities.

The theory of the action of an alternating magnetic field on a movable coil conveying a current of the same frequency is discussed in the second part of the paper; and the application of such theory to shunt magnet instruments is given in the third part. The final portion deals with experimental verification.

Part I.—THE MATHEMATICAL RELATIONSHIPS OF CYCLIC QUANTITIES.

We shall use heavy letters such as **A**, **B**, **C**, to denote single valued cyclic functions of the variable t , and the corresponding letters in lighter type, *A*, *B*, *C*, to denote the square root of mean square values of **A**, **B**, **C**, respectively. \overline{A} we define as the *magnitude* of **A**, and will be a constant as regards t . The mean value of the product of two quantities such as **A**, **B**, will be represented by \overline{AB} , so that $A^2 = \overline{A \cdot A} = \overline{A}^2$.

Any cyclic quantity **A** must either have its mean value zero, when it may be described as *alternating*, or it must consist of the sum of two parts, one of which is *steady* and the other *alternating*. With few exceptions the quantities occurring in actual alternate current problems are alternating in the above sense. The differential coefficient of any cyclic quantity is necessarily alternating. The integral of a cyclic quantity is not met with unless its mean or steady value is zero, and as this integral will in most actual cases also have zero mean value it will be as definite a quantity as that of a differential coefficient. The product of two cyclic quantities such as a voltage **V** and a current **A** consists in general of two portions, one of which is steady and the other alternating. These parts correspond precisely with the scalar and vector products of two vectors.

Whatever cyclic quantities **A** and **B** may be if we consider the mean values of the two identical expressions

$$\left(\frac{\mathbf{A}}{A} - \frac{\mathbf{B}}{B}\right)^2 \equiv \frac{\mathbf{A}^2}{A^2} + \frac{\mathbf{B}^2}{B^2} - 2\frac{\mathbf{AB}}{AB},$$

we see that these mean values can only be zero when **A** is proportional to **B** for *each instant* of the cycle, and also that we can always find a *real* angle ϕ such that

$$(1) \quad \overline{AB} = AB \cos \phi.$$

The value of ϕ determined from this equation may be defined as the *phase*

* 'Roy. Soc. Proc.,' vol. 49, March, 1891.

difference of the quantities A and B . These quantities will be said to be *in phase* when ϕ is zero, and this can only happen when the ratio of A to B is independent of the time t . They will be said to be *in quadrature* when $\cos \phi$ is zero, that is, when the mean product of A and B is zero.

For any two quantities A and N it is always possible to consider either of them, say N , as the sum of two quantities the first of which is in phase with A and the second in quadrature with it, for we can so define n that

$$(2) \quad N = LA + n,$$

where L is a quantity, independent of time, which we can so choose that n and A are in quadrature. It readily follows that the magnitudes of the three quantities in (2) can be denoted by the lengths of the three sides of a right-angled triangle, and that the angle between any two sides of this triangle is the phase difference of the corresponding quantities. The mode of proof merely involves the process of multiplying the equation by some cyclic quantity and taking means. By successive application of this process, it is possible to establish the following theorem:—

Each one of a number of known cyclic quantities, however different these may be in wave form, can be expressed as a linear function of an equal number of other cyclic quantities, these latter being such that the mean square of each is unity and the mean product of any two is zero.

Thus, if there are n cyclic quantities A_1, A_2, \dots, A_n , we can always find other cyclic quantities, X_1, X_2, \dots, X_n , each of which is of unit magnitude, each two of which are in quadrature, and which are such as to satisfy the identities

$$(3) \quad \begin{aligned} A_1 &\equiv A_1 X_1 \\ A_2 &\equiv A_2 [X_1 \cos \alpha_{21} + X_2 \cos \alpha_{22}] \\ &\dots\dots\dots \\ A_n &\equiv A_n [X_1 \cos \alpha_{n1} + X_2 \cos \alpha_{n2} + \dots + X_n \cos \alpha_{nn}], \end{aligned}$$

where A_m is the magnitude of A_m , and where

$$(4) \quad 1 = \cos^2 \alpha_{m1} + \cos^2 \alpha_{m2} + \dots + \cos^2 \alpha_{mm}$$

for every value of m from 1 to n .

The quantities α are perfectly determined by the magnitudes and phase differences of the quantities A . Indeed, α_{rs} is the phase difference between A_r and X_s , so that if the system of equations (3) has been established as far as, say, A_3 , the quantities X_1, X_2, X_3 are known; the phase differences between these and A_4 can be calculated, determining $\alpha_{41}, \alpha_{42}, \alpha_{43}$; the equation for A_4 , constituting the definition of X_4 , can then be used to show that X_4 is in quadrature with each of the quantities X_1, X_2, X_3 ; equation (4) for $m = 4$ determines α_{44} ; and so on.

If three quantities, A_1 , A_2 , A_3 , of different wave form, together with linear functions of these quantities, comprise all the cyclic functions which have to be considered, it is possible, as previously shown,* to represent the magnitudes and phase relationships of all such quantities by a vector figure drawn in three dimensions. This is not possible when four independent wave forms are involved, but in all cases it is possible to establish the system of equations (3) and (4).

Important alternate current problems involve so many quantities, and the relationship between these is so complicated by the effects of varying permeability, hysteresis, irregular wave forms, etc., that mathematically accurate representation is impossible with a simpler system of equations than is indicated in (3). In practice, however, great simplification results from two considerations. In the first place, although the quantities involved may be very numerous, it is only necessary, as a rule, to consider the mutual relations of two or three of them at any one time, and it is in general possible to construct the vector figure actually needed for this purpose. In the second place, the figure can in all cases be reduced to a two-dimensioned figure by projection, as illustrated by figs. 1, 2, and 3 below. Each quantity involved can be reduced to one of the forms

$$\mathbf{R} = R[\mathbf{x} \cos \phi + \mathbf{y} \sin \phi],$$

$$\mathbf{S} = S[\mathbf{x} \cos \alpha + \mathbf{y} \cos \beta + \mathbf{z} \cos \gamma],$$

where \mathbf{x} and \mathbf{y} are cyclic quantities in quadrature, the same for all the quantities \mathbf{R} , \mathbf{S} , and where each quantity \mathbf{z} is in quadrature both with \mathbf{x} and \mathbf{y} . The projection of \mathbf{S} , denoted by \mathbf{S}_1 , is

$$\mathbf{S}_1 = S[\mathbf{x} \cos \alpha + \mathbf{y} \cos \beta].$$

It is possible to represent all the quantities \mathbf{R} , \mathbf{S}_1 , by vectors in a plane, and it is always true that

$$(5) \quad \overline{\mathbf{RS}} = \overline{\mathbf{RS}_1}.$$

The plane figure so constructed will in most cases meet all requirements.

It is frequently necessary to consider quantities like \mathbf{N} and $\dot{\mathbf{N}}$, such that one is the differential coefficient of the other. Newton's notation may be conveniently used, not only for the instantaneous values \mathbf{N} , $\dot{\mathbf{N}}$, but also for the corresponding magnitudes N , \dot{N} , since the latter are constants as regards time, so that no ambiguity can arise.

If \mathbf{A} and \mathbf{B} are any two cyclic quantities, it will be readily seen that

$$(6) \quad \overline{\mathbf{A}\dot{\mathbf{B}}} = -\overline{\mathbf{B}\dot{\mathbf{A}}}, \quad \overline{\mathbf{A}\dot{\mathbf{A}}} = 0.$$

* 'Roy. Soc. Proc.,' vol. 61, p. 465.

It follows from (2), that for any two quantities \mathbf{N} and \mathbf{A} we can so choose \mathbf{L} that a right-angled vector triangle is denoted by the equation

$$(i) \quad \mathbf{N} = \mathbf{L}\mathbf{A} + \mathbf{n}.$$

From this we have

$$(ii) \quad \dot{\mathbf{N}} = \mathbf{L}\dot{\mathbf{A}} + \dot{\mathbf{n}}$$

and

$$(iii) \quad \dot{\mathbf{N}}_1 = \mathbf{L}\dot{\mathbf{A}}_1 + \dot{\mathbf{n}}_1.$$

The triangle represented by (iii) is the projection of that denoted by (ii) on the plane determined by (i) or by \mathbf{N} , \mathbf{A} , and \mathbf{n} . By making use of (5), it can be seen that the plane vectors involved in the above equations are

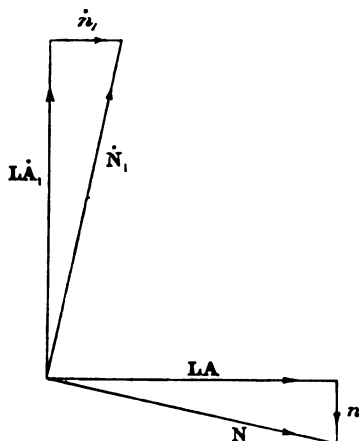


FIG. 1.

represented, as in fig. 1, by two similar right-angled triangles with corresponding sides perpendicular.

It follows that—

(7) If \mathbf{N} and \mathbf{A} are any two cyclic quantities represented by vectors in a plane, the vector projections of $\dot{\mathbf{N}}$ and $\dot{\mathbf{A}}$ on the same plane will be obtained by turning each of the vectors \mathbf{N} and \mathbf{A} through a right angle in the same sense, and by increasing their magnitudes in the same proportion.

We might similarly represent $\dot{\mathbf{N}}$, $\dot{\mathbf{A}}$, and $\dot{\mathbf{n}}$ by vectors in a plane, and project on to this plane vectors denoting \mathbf{N} , \mathbf{A} , and \mathbf{n} , and also those denoting $\dot{\mathbf{N}}$, $\dot{\mathbf{A}}$, and $\dot{\mathbf{n}}$. Representing the projected vectors by the suffix unity, we have fig. 2, consisting of three similar right-angled triangles. $\dot{\mathbf{N}}_1$ will be represented by a vector in the same direction as, but drawn in the opposite sense to, that which represents \mathbf{N}_1 . This will also be true of the vectors $\dot{\mathbf{A}}_1$ and \mathbf{A}_1 , etc. Of course, the actual magnitude of $\dot{\mathbf{N}}$ will bear to that of \mathbf{N} a ratio which is dependent on the wave form of \mathbf{N} , and this ratio will not necessarily be the same as that of the magnitudes of $\dot{\mathbf{A}}$ and \mathbf{A} , two other

quantities related in the same way. Indeed, this ratio is not the same for $\ddot{\mathbf{N}}$ and $\dot{\mathbf{N}}$ as it is for $\dot{\mathbf{N}}$ and \mathbf{N} , except in the special case in which each follows the simple sine law denoted by $\dot{\mathbf{N}} = -p^2\mathbf{N}$.

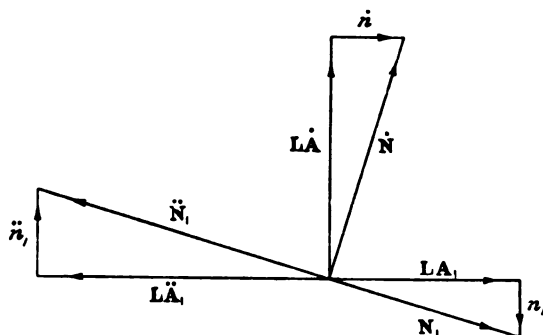


FIG. 2.

In other cases it can easily be established by aid of the theorems denoted by (1) and (6) that

$$(8) \quad \begin{cases} \mathbf{N} : \dot{\mathbf{N}} : \ddot{\mathbf{N}} : \ddot{\ddot{\mathbf{N}}}, \text{ etc.}, \\ = 1 : p_1 : p_1 p_2 : p_1 p_2 p_3, \text{ etc.} \\ \text{where } p_1 < p_2 < p_3, \text{ etc.} \end{cases}$$

It is also easy to show that

$$(9) \quad \ddot{\mathbf{N}} = -p_1^2\mathbf{N} + \mathbf{Z} \quad \text{and} \quad \ddot{\mathbf{N}}_1 = -p_1^2\mathbf{N},$$

where \mathbf{Z} is in quadrature with both \mathbf{N} and $\dot{\mathbf{N}}$, and where $\ddot{\mathbf{N}}_1$ is the projection of $\ddot{\mathbf{N}}$ on the plane containing \mathbf{N} and $\dot{\mathbf{N}}$.

Part II.—THE ACTION OF A CYCLIC MAGNETIC FIELD ON A MOVABLE COIL CONVEYING A CURRENT OF THE SAME FREQUENCY.

If \mathbf{C} be the current traversing a coil, the flux through which is \mathbf{F} (the flux per turn multiplied by the number of turns), and if θ be an angular displacement, the corresponding torque \mathbf{T} will be given by

$$(10) \quad \mathbf{T} = \mathbf{C} \frac{d\mathbf{F}}{d\theta}.$$

If the current \mathbf{C} and the flux \mathbf{F} are steady, the torque due to their interaction (by the convenient rule due to Maxwell, vol. II, § 489) will be so directed as to tend to increase \mathbf{F} , provided we consider \mathbf{F} as positive when threading the coil in the same direction as the flux due to the current \mathbf{C} . If we choose a particular direction round the coil as positive for \mathbf{C} , this fixes the positive direction of \mathbf{F} , and the direction of \mathbf{T} , which is to be con-

sidered positive, is that corresponding with such a displacement $d\theta$ that F increases with the displacement. If the current C and the flux F are alternating, the above statements are still true at any instant, but it does not follow that the average or steady value of T is such as to turn the coil so as to increase the *magnitude* of F , that is to say, so as to increase the square root of the time average of F^2 . The mean value of the product determining T will be zero when C and F are in quadrature, and will change sign as the phase difference alters from just below, to just above, a right angle.

If F is entirely due to C , that is, if $F = LC$, where L is the self-inductance of the coil, we have

$$(11) \quad T = C^2 \frac{dL}{d\theta},$$

and is necessarily positive, that is, T is so directed that the displacement it tends to produce is such as to increase L . This torque always exists whatever may be the cause of the current C , but, in the cases we shall have to consider, it is so small as to be negligible.

We shall in all cases assume that the magnetic field, though varying with the time, has a fixed mode of distribution in space, or that the induction density at any point is the product of a vector function determined by the position of the point and not dependent on the time, and a scalar function of the time, the same for all points in the field. In other words, we shall assume that the fluxes through any two coils placed anywhere in the field are always in the same *phase*, though the *magnitude* of each flux depends on the configuration of the coil, and on the co-ordinates determining its position. Alternate currents of commercial frequencies vary so slowly that this assumption is justifiable, except in a few cases in which the variable permeability and hysteresis of iron prevent the medium from having a fixed magnetic character, and cause the flux distribution to alter for different magnetising currents.

If the position of the coil is completely determined by θ , we have, on the above assumptions,

$$F = F\tau,$$

where F depends solely on θ and τ depends solely on the time. Thus

$$T = C \frac{dF}{d\theta} = C\tau \frac{dF}{d\theta},$$

or

$$(12) \quad T = \frac{1}{F} \frac{dF}{d\theta} CF.$$

Thus the mean value, or the steady part, of \mathbf{T} , which we shall denote by \mathbf{T}_s , is given by

$$(13) \quad \mathbf{T}_s = \frac{1}{\mathbf{F}} \frac{d\mathbf{F}}{d\theta} \overline{\mathbf{C}\mathbf{F}};$$

and this equation must be true in all cases.

Now if the current is \mathbf{C}_1 , due to the electromotive force induced by the time rate of change of the moving coil flux \mathbf{F} , the torque which results will depend on the nature of the circuit containing this coil.

Suppose this circuit to be metallically closed, and to have a resistance \mathbf{R} and self-inductance \mathbf{L} , we then have

$$(14) \quad \mathbf{R}\mathbf{C}_1 + \mathbf{L}\dot{\mathbf{C}}_1 = -\dot{\mathbf{F}}.$$

Multiply this by \mathbf{F} and take means. We get

$$\overline{\mathbf{R}\mathbf{C}_1\mathbf{F}} + \overline{\mathbf{L}\dot{\mathbf{C}}_1\mathbf{F}} = -\overline{\mathbf{F}\dot{\mathbf{F}}} = 0;$$

but if we multiply the same equation by $\mathbf{L}\mathbf{C}_1$ and take means, we get

$$\overline{\mathbf{L}\mathbf{R}\mathbf{C}_1^2} + \overline{\mathbf{L}^2\mathbf{C}_1\dot{\mathbf{C}}_1} = -\overline{\mathbf{L}\mathbf{C}_1\dot{\mathbf{F}}},$$

or, using (6),

$$\overline{\mathbf{L}\mathbf{R}\mathbf{C}_1^2} + 0 = +\overline{\mathbf{L}\dot{\mathbf{C}}_1\mathbf{F}}.$$

By adding these two derived equations, we get, on dividing by \mathbf{R} ,

$$\overline{\mathbf{L}\mathbf{C}_1^2} + \overline{\mathbf{C}_1\dot{\mathbf{F}}} = 0.$$

Hence, substituting in (13), we get

$$(15) \quad \mathbf{T}_s = -\frac{1}{\mathbf{F}} \frac{d\mathbf{F}}{d\theta} \overline{\mathbf{L}\mathbf{C}_1^2}.$$

From this it follows that \mathbf{T}_s is negative, or

(16) *A closed conducting circuit having self-inductance and placed in an alternating magnetic field will tend to set itself so as to decrease to a minimum the magnitude of the flux it surrounds.*

The forces tending to displace the coil vanish if \mathbf{L} is zero or negligible, but they are not simply proportional to \mathbf{L} , since \mathbf{C}_1 is inversely proportional to the impedance of the coil.

Suppose in the next place that the circuit of the coil is closed through a condenser of capacity \mathbf{K} . If the resistance of the circuit is \mathbf{R} , the current \mathbf{C}_1 induced by the field will, under ordinary circumstances, be so small that $\mathbf{R}\mathbf{C}_1$ is negligible in comparison with $\dot{\mathbf{F}}$. Under these conditions, if \mathbf{V}_1 is the voltage of the condenser we find, after paying due regard to sign, that,

$$\mathbf{C}_1 = \mathbf{K}\dot{\mathbf{V}}_1 \quad \text{and} \quad \mathbf{V}_1 = -\dot{\mathbf{F}},$$

whence $\overline{\mathbf{C}_1\mathbf{F}} = \mathbf{K}\overline{\dot{\mathbf{V}}_1\mathbf{F}} = -\mathbf{K}\overline{\mathbf{V}_1\dot{\mathbf{F}}} = +\mathbf{K}\overline{\mathbf{V}_1^2} = \mathbf{K}\mathbf{V}_1^2;$

so that, using (13), we have in this case

$$(17) \quad T_s = +\frac{1}{F} \frac{dF}{d\theta} K V_1^2,$$

where V_1 is the voltage induced in the circuit by the field; thus T_s is necessarily positive, or we have

(18) *If a coil whose circuit is closed through a condenser be placed in an alternating magnetic field, it will tend to move so as to increase to a maximum the magnitude of the flux it surrounds.*

It can be shown that (17) is accurate, even allowing for the resistance of the coil, though in this case the voltage V_1 of the condenser is not the same as $-\dot{F}$ the electromotive force induced by the field. Allowing for the resistance R , it will be found that

$$C_1 = K \dot{V}_1, \quad V_1 + R C_1 = -\dot{F}.$$

From these equations we obtain

$$\begin{aligned} \overline{C_1 V_1} &= K \overline{V_1 \dot{V}_1} = 0, \\ \overline{C_1 \dot{F}} &= K \overline{\dot{V}_1 \dot{F}} = -K \overline{V_1 \ddot{F}} = +K \overline{V_1 (V_1 + R C_1)} \\ &= K \overline{V_1^2} = K V_1^2, \end{aligned}$$

as in the previous case, while the power supplied to the circuit is

$$\overline{C_1 (-\dot{F})} = \overline{C_1 (V_1 + R C_1)} = R C_1^2$$

and

$$\dot{F}^2 = V_1^2 + R^2 C_1^2,$$

so that if $R C_1$ is less than one per cent. of \dot{F} , the values of V_1^2 and \dot{F}^2 will differ by less than 1 part in 10,000.

Now let us suppose we have constructed an instrument for alternate current measurements, consisting of a movable coil placed in the intense alternating magnetic field due to an iron-cored electromagnet, and let us assume that the circuit of the coil includes a portion, external to the instrument, on which an alternating electromotive force E is impressed. The torque acting on the coil will still be given by (13), where F is the flux through the coil due to the electromagnet, and where C is the resultant current through the coil, due to all the impressed and reactive electromotive forces in the circuit.

Let us assume in the first place that the moving coil circuit is metallically closed, and that its resistance is R and its self-inductance L . We then have for the moving coil current

$$(19) \quad R C + L \dot{C} = -\dot{F} + E.$$

The solution of this is $C = C_1 + C_2$,

where $R C_1 + L \dot{C}_1 = -\dot{F}, \quad R C_2 + L \dot{C}_2 = E,$

so that the torque is

$$T_s = \frac{1}{F} \frac{dF}{d\theta} \overline{CF} = \frac{1}{F} \frac{dF}{d\theta} (\overline{C_1 F} + \overline{C_2 F}),$$

or

$$T_s = T_1 + T_2,$$

where T_1 is the torque already calculated (15) which depends on F , and is independent of E , while T_2 is a torque due to the interaction of F with C_2 , a current calculated from E alone, without reference to F , or to its reactive influence on the circuit.

A similar argument applies to the case in which the moving coil is closed through a condenser. In this case we have the equations

$$(20) \quad C = K\dot{V} \quad \text{and} \quad V + RC + L\dot{C} = -\dot{F} + E,$$

and we can put

$$C = C_1 + C_2 \quad \text{and} \quad V = V_1 + V_2, \text{ etc.,}$$

where the quantities having the first suffix satisfy the equations when E is zero, and those with the second suffix satisfy the equations when \dot{F} is put equal to zero. As in the previous case, the torque T_s on the moving coil will consist of two independent parts, one of which T_1 is solely due to F , and the other of which T_2 is due to C_2 and F , where C_2 is solely due to E . In each case the importance or otherwise of T_1 can easily be tested in an actual instrument by simply arranging for E to be zero. As shown later, T_1 can also be easily calculated from the formula.

The method of superposition can be conveniently applied to alternate current problems provided, (1) the differential equations connecting the currents and voltages are linear, and (2) the resistances, induction coefficients, capacities and other factors are independent, not only of the time, but also of the physical variables, such as current, voltage, etc. Under these conditions it is easy to prove the following theorem:—

(21) If E_1, E_2, E_3 , etc., be *any* impressed electromotive forces distributed in *any* manner among the branches of *any* network of conductors, the current C in *any* selected branch will be given *at each instant* by the equation

$$C = C_1 + C_2 + C_3 + \dots,$$

where C_1 is the current calculated on the assumption that all the impressed electromotive forces are zero except E_1 , and similarly for C_2, C_3 , etc. The current in any branch is at every instant the sum of the currents which would be produced in that branch by each impressed electromotive force acting alone.

Since the current in any branch can theoretically always be reduced to zero by inserting a suitable electromotive force into the branch, the above theorem may readily be used to prove that.

(22) If the electromotive forces impressed on a network cause a difference of potential V between two given points of the network, and if these two points be afterwards joined by a wire possessing resistance and self (but not mutual) inductance, the current which will flow through the wire will be exactly what an electromotive force V would produce in a circuit consisting of the wire, and the network to which the wire is joined, assuming the other impressed electromotive forces removed from the network.

The above theorems I have found serviceable in reasoning out the behaviour of connecting networks used for a number of tests made in connection with the present paper. The complete mathematical solution of the problems presented by such networks is, as a rule, impossible, owing to the unknown wave forms of the variables. For the purpose of an actual test the complete solution is not, as a rule, needed, while the particular relationship required can often be readily seen with the aid of the above theorems* without making any assumptions about wave form.

Part III.—THE THEORY OF SHUNT MAGNET INSTRUMENTS.

Let r be the resistance of the coil of an electromagnet subjected to a periodic voltage V , and let N be the total number of lines of force enclosed by the winding, that is let N be the product of the number of turns of the coil and the flux of lines through the core. Let A_m be the current flowing through the coil. We then have

$$(23) \quad V = rA_m + \dot{N}.$$

For the cores of large transformers with closed magnetic circuits it is in some cases the fact that the magnitude of V is over one hundred thousand times as great as that of rA_m . For small magnetic circuits suitable for instruments of ordinary size the ratio will be much less, especially if an air gap is introduced to allow a coil to move across the field, but even in such cases I have found it possible with careful design to make this ratio exceed 250 for alternate currents having a frequency of 50 cycles per second.

Let us for the present assume r to be so small that rA_m is negligible compared with V , or that the ratio of the resistance to the impedance of the coil is negligible. The relationship between the field N and the exciting voltage V is then *independent of the permeability and hysteresis of the core*. Suppose the electromagnet to have a narrow air gap in which a coil can move,

* The truth of (21) and (22) for *direct current circuits* has been long known. The latter theorem (22) is due to Thévenin, 'Comptes Rendus,' 1888, vol. 97, p. 159, and is often convenient. Theorem (21) for *alternate current circuits*, though not precisely stated, seems more or less indicated in one of Heaviside's 'Electrical Papers,' vol. 2, pp. 294—296.

so as to turn about an axis, its position being completely specified by a deflection θ . Let \mathbf{F} be the flux enclosed by this coil for the deflection θ . We assume \mathbf{F} strictly in phase with \mathbf{N} , so that

$$(24) \quad \mathbf{F} = \rho \mathbf{N},$$

where ρ depends on θ , but is independent of time. Hence, assuming r in (24) negligible, we have

$$(25) \quad \dot{\mathbf{F}} = \rho \dot{\mathbf{N}} = \rho \mathbf{V},$$

so that ρ is the ratio of the voltage of the moving coil (on open circuit) to the applied voltage V , and is a quantity which for any deflection θ can be measured, provided suitable voltmeters are available.

Suppose the moving coil circuit be closed through a condenser of capacity K , and to have an electromotive force \mathbf{E} impressed upon it, or suppose the moving coil (in series with the condenser K) be applied to mains at potential \mathbf{E} , we then have, from (20), assuming R and L negligible,

$$\mathbf{C} = K \dot{\mathbf{V}}, \quad \text{where} \quad \mathbf{V}_1 = -\dot{\mathbf{F}} + \mathbf{E} = -\rho \mathbf{V} + \mathbf{E},$$

so that

$$\mathbf{C} = -K\rho \dot{\mathbf{V}} + K\dot{\mathbf{E}}.$$

Hence

$$\begin{aligned} \overline{\mathbf{F}\mathbf{C}} &= -K\rho \overline{\mathbf{V}\dot{\mathbf{F}}} + K\overline{\mathbf{E}\dot{\mathbf{F}}} \\ &= +K\rho \overline{\mathbf{V}\dot{\mathbf{F}}} - K\overline{\mathbf{E}\dot{\mathbf{F}}}; \end{aligned}$$

and by (25) this is equal to

$$\overline{\mathbf{F}\mathbf{C}} = K\rho [\rho \overline{\mathbf{V}^2} - \overline{\mathbf{E}\mathbf{V}}].$$

For a voltmeter we can make \mathbf{E} the same as \mathbf{V} , but we can apply it to the moving coil in either of two ways. Thus for a voltmeter

$$(26) \quad \overline{\mathbf{F}\mathbf{C}} = K\rho(\rho \pm 1) V^2.$$

This quantity is proportional to the torque, and hence this torque for a given value of θ and of ρ simply depends on V^2 , so that the instrument can be calibrated as a voltmeter. It is easily possible to make ρ negligible compared with unity, but in any case the factor $[\rho \pm 1]$ only affects the calibration, and not the accuracy of the voltmeter. It readily follows from (24), remembering that \mathbf{N} is independent of θ , that

$$(27) \quad \begin{aligned} \mathbf{F} &= \rho \mathbf{N}, \\ \text{and} \quad \frac{1}{\mathbf{F}} \frac{d\mathbf{F}}{d\theta} &= \frac{1}{\rho} \frac{d\rho}{d\theta}, \end{aligned}$$

so that the general expression (13) for the steady torque is the same as

$$(28) \quad T_s = \frac{1}{\rho} \frac{d\rho}{d\theta} \overline{\mathbf{C}\mathbf{F}} = \frac{d\rho}{d\theta} \overline{\mathbf{C}\mathbf{N}},$$

which in the case of the above voltmeter (with ρ negligible compared with unity) becomes

$$(29) \quad T_s = \pm \frac{d\rho}{d\theta} KV^2.$$

Next assume the moving coil circuit to be metallically closed through the secondary of a transformer the coils of which have a constant mutual inductance M . Suppose the primary coil of this transformer to be traversed by a current A . Let R be the resistance of the moving coil circuit, but for the present let us assume the self-inductance of this circuit negligible. We then have

$$RC = -\dot{F} + E, \text{ where } E = MA.$$

Also by (25)

$$\dot{F} = \rho V,$$

and by (13) and (28)

$$T_s = \frac{1}{\rho} \frac{d\rho}{d\theta} \overline{CF}.$$

But

$$\begin{aligned} \overline{RCF} &= -\overline{FF} + \overline{EF} = \overline{MAF} \\ &= -\overline{MA\dot{F}} = -M\rho \overline{AV}, \end{aligned}$$

so that

$$(30) \quad T_s = \pm \frac{d\rho}{d\theta} \frac{M}{R} \overline{AV},$$

or T_s is a measure of the power in watts associated with the current A and the voltage V . The ambiguity of sign merely implies that the secondary of the transformer can be connected up in two ways.

Certain assumptions have been made in establishing the formulæ (29) and (30), and it remains to show what influence any error in these assumptions has on the action of the instrument.

I have already discussed the theory and construction of iron cored shunt magnet instruments, and described a rather long experimental investigation of their behaviour, in two papers published by the Institution of Electrical Engineers (vols. 34 and 36). In one of these papers the theory of the voltmeter, and of its error, were very fully dealt with, and it will suffice to add here that these voltmeters are most satisfactory instruments. They need but a negligibly small current to work them, and are very sensitive, especially when constructed so as to have a weak control, and for use with an optical pointer.

The theory of the wattmeter merits much fuller consideration. The properties of magnetic fields due to shunt excited electromagnets have a wider interest than that arising from the use of these magnets for a particular purpose, such as that of a voltmeter or a wattmeter. If a magnetic field can be caused and controlled by an applied voltage in accord-

ance with a strict mathematical law [by which is meant a law which in essence involves no factors dependent upon the magnetic or other variable physical properties of the medium, and which, therefore, is independent of changes in these physical properties], such a field must be found useful, sooner or later, for a variety of measuring purposes. No more searching test can well be applied to such a field than an investigation of its action in connection with a wattmeter, for no other electrical instrument is required to work under such severe conditions. Its indications must be correct for all values of no fewer than five variables, viz., amperes, volts, power factor, frequency, and wave form. Moreover, while the deflecting forces corresponding with the power to be measured diminish with the power factor of the load, this is not the case with those corresponding with the error of the instrument. The true power for a given current and voltage is proportional to $\cos \phi$, while the most important part of the error is proportional to $\sin \phi$, so that this actually increases as $\cos \phi$ diminishes, and becomes relatively very important for low power factors.

Now to determine T , we have, besides (28), the equations

$$(31) \quad \begin{aligned} \mathbf{V} &= r\mathbf{A}_m + \dot{\mathbf{N}} & \mathbf{F} &= \rho\mathbf{N}, \\ \mathbf{RC} + \mathbf{LC} &= -\dot{\mathbf{F}} + \mathbf{E}. \end{aligned}$$

\mathbf{E} is the electromotive force in the secondary of the transformer the primary of which is traversed by the main current \mathbf{A} . For an air core transformer \mathbf{E} will be strictly proportional to \mathbf{A} . If the magnetic circuit of the transformer contains iron, the flux \mathbf{N}_a enclosed by the secondary coil will not be strictly proportional to \mathbf{A} , but we can always put (see (2))

$$(32) \quad \mathbf{N}_a = M\mathbf{A} + \mathbf{n},$$

where \mathbf{n} is in quadrature with \mathbf{A} and

$$\mathbf{E} = \dot{\mathbf{N}}_a = M\dot{\mathbf{A}} + \dot{\mathbf{n}}.$$

From the above equations (31) we can omit $\dot{\mathbf{F}}$, since, as already shown (19 and 15), we can calculate the part of T , due to $\dot{\mathbf{F}}$ separately. Its value will be

$$T_1 = -\frac{1}{\rho} \frac{d\rho}{d\theta} LC_1^2,$$

where C_1 is calculated from

$$\mathbf{RC}_1 + \mathbf{LC}_1 = -\dot{\mathbf{F}},$$

or since \mathbf{C}_1 and $\dot{\mathbf{C}}_1$ are in quadrature and the ratio of the magnitudes of \mathbf{LC}_1 and \mathbf{RC}_1 is very small,

$$R^2 C_1^2 = \dot{\mathbf{F}}^2 = \rho^2 V^2$$

with sufficient accuracy. Hence the torque due to $\dot{\mathbf{F}}$ is

$$(33) \quad T_1 = -\rho \frac{d\rho}{d\theta} L \frac{V^2}{R^2},$$

a quantity determined by V alone. It is not dependent on A or on the power factor of the load, nor is it dependent upon the frequency or wave form of V , assuming rA_m is negligible. If we omit $\dot{\mathbf{F}}$ from equations (31), these become

$$(34) \quad \begin{aligned} \mathbf{V} &= r\mathbf{A}_m + \dot{\mathbf{N}}, & \mathbf{F} &= \rho\mathbf{N}, \\ \mathbf{RC} + \mathbf{L}\dot{\mathbf{C}} &= \mathbf{M}\dot{\mathbf{A}} + \mathbf{n} = \dot{\mathbf{N}}_a. \end{aligned}$$

The above may be regarded as equations between vectors, and remembering (7) and the quadrature relationship of vectors like \mathbf{C} and $\dot{\mathbf{C}}$, the complete figure can be easily indicated as in fig. 3, where ϕ is the phase difference of the current \mathbf{A} and the main voltage \mathbf{V} , and the small phase errors of the instrument, which for the sake of clearness are greatly exaggerated in the figure, are denoted as follows:—

$$(35) \quad \begin{array}{llll} \phi_m, & \text{the angle between } \dot{\mathbf{N}} \text{ and } \mathbf{V} & \text{due to the resistance of the magnet} \\ & & \text{coil.} \\ \phi_s, & \text{,, ,, } \dot{\mathbf{N}}_a \text{ and } \mathbf{C} & \text{,, self-inductance of the} \\ & & \text{moving coil circuit.} \\ \phi_i, & \text{,, ,, } \mathbf{N}_a \text{ and } \mathbf{A} & \text{,, hysteresis of the trans-} \\ & & \text{former core.} \end{array}$$

These angles must each be made very small if the wattmeter is to be even approximately correct, so that we shall regard them as small quantities of the first order, and neglect their squares and products compared with unity. Hence it follows, with the aid of (34), that to this degree of approximation

$$\begin{aligned} \mathbf{RC} &= \mathbf{M}\dot{\mathbf{A}} = \mathbf{M}p\mathbf{A}, & \mathbf{V} &= \dot{\mathbf{N}} = \mathbf{N}p, \\ \mathbf{F} &= \rho\mathbf{N} \quad \text{or} \quad \mathbf{F}p = \rho\mathbf{V}, \end{aligned}$$

and that these magnitudes are the same as if ϕ_m, ϕ_s, ϕ_i , were all zero.

Now the torque depends upon $\overline{\mathbf{F}\mathbf{C}}$, that is upon $\mathbf{FC} \cos(\phi + \phi_s)$, where $(\phi + \phi_s)$ is the phase difference between \mathbf{F} and \mathbf{C} . The magnitudes \mathbf{F} and \mathbf{C} are the same as if the phase errors were zero. It will be seen from fig. 3, assuming as a first approximation that all the vectors lie in one plane, that $(\phi + \phi_s)$ is the complement of the angle separating \mathbf{C} and $\dot{\mathbf{N}}$, since $\dot{\mathbf{N}}$ is in quadrature with \mathbf{N} and \mathbf{F} . Hence

$$\phi + \phi_s = \phi + \phi_m + \phi_s + \phi_i,$$

and, since all the phase errors are small,

$$\cos(\phi + \phi_s) = \cos\phi(1 - \phi_s \tan\phi),$$

$$(36) \quad \text{where } \phi_s = \phi_m + \phi_s + \phi_i,$$

Hence, by (28), (31), and (33), the complete expression for T_s is

$$(37) \quad T_s = \pm \frac{d\rho}{d\theta} \frac{\mathbf{M}}{\mathbf{R}} \mathbf{W}(1 - \phi_s \tan\phi) - \rho \frac{d\rho}{d\theta} \mathbf{L} \frac{\mathbf{V}^2}{\mathbf{R}^2},$$

indicate a shorter proof in which advantage is taken of the smallness of the fractions denoting the phase errors.

The value of T_s must evidently be a function of V , A , ϕ , and the phase errors, and, hence, if we can neglect squares and products of the latter, we can, by Taylor's theorem, expand T_s and put

$$T_s = {}_0T_s [1 + \lambda \phi_m + \mu \phi_s + \nu \phi_i],$$

where ${}_0T_s$ is the value of T_s , assuming all the phase errors to be zero, and where λ , μ , ν do not involve these quantities. It only remains to determine the values of these coefficients, and it is clear that we can find any one of them by assuming two of the quantities r , L , n equal to zero, and solving the equations (34) so modified. It is easy to show that each coefficient can be expressed by the formula

$$-(1 - \epsilon^2) \tan \phi,$$

where ϵ^2 is a positive quantity, which may be zero, which is always very small, and which, in fact, can nearly always be neglected.

Thus, to find λ , the coefficient of ϕ_m , we put L and n each equal to zero in (34), and have the equations

$$\mathbf{V} = r\mathbf{A} + \dot{\mathbf{N}}; \quad R\mathbf{C} = M\dot{\mathbf{A}}; \quad \text{and} \quad \mathbf{F} = \rho\mathbf{N}.$$

Thus

$$\begin{aligned} \overline{\mathbf{FC}} &= \rho \frac{M}{R} \overline{\mathbf{NA}} = -\rho \frac{M}{R} \overline{\mathbf{NA}} \\ &= -\rho \frac{M}{R} \dot{\mathbf{N}}A \cos(\phi + \phi_m'), \end{aligned}$$

where $\phi + \phi_m'$ is the angle between the vectors \mathbf{A} and $\dot{\mathbf{N}}$. Referring to fig. 3, it will be seen that though the vectors $\dot{\mathbf{N}}$, \mathbf{V} , and \mathbf{A} may not lie in one plane, they can be properly represented in a three-dimensioned figure, and that $\phi + \phi_m'$ cannot exceed $\phi + \phi_m$, and must, in general, be less, or the ratio of ϕ_m' to ϕ_m must be less than unity. Also the magnitudes V and \dot{N} must be equal, since ϕ_m is small and A_m is approximately perpendicular to V . In other words, \dot{N} is independent of ϕ_m , and it readily follows that

$$T_s = {}_0T_s \frac{\cos(\phi + \phi_m')}{\cos \phi} = {}_0T_s [1 - \phi_m' \tan \phi],$$

so that

$$\lambda = -\frac{\phi_m' \tan \phi}{\phi_m} = -(1 - \epsilon^2) \tan \phi.$$

By a similar process the coefficients μ and ν may be obtained, and their values will be found to satisfy a similar formula. The result is to completely establish (36) and (37) with the limitation already stated in regard to the former equation; that it must be regarded as a vector

equation, so that ϕ_r can never be greater, and must, in general, be less than the numerical sum of ϕ_m , ϕ_s , and ϕ_i .

Part IV.—EXPERIMENTAL VERIFICATION.

A moving coil electromagnet instrument, having the characteristics already described, may be constructed of thin sheet iron stampings, as illustrated in fig. 5, in which shaded areas denote the windings in section. The magnetic circuit contains only one air gap. To reduce the reluctance of this as much as possible, its section is increased by extending the poles, so that one almost surrounds the other as shown. The polar distance across the gap is reduced to the smallest value consistent with the free motion of the moving coil. This coil is rectangular in shape, and turns about one

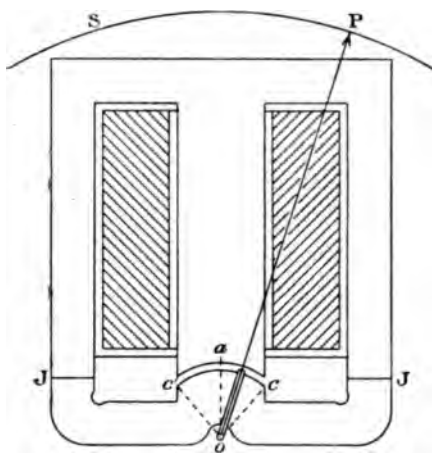


FIG. 4.

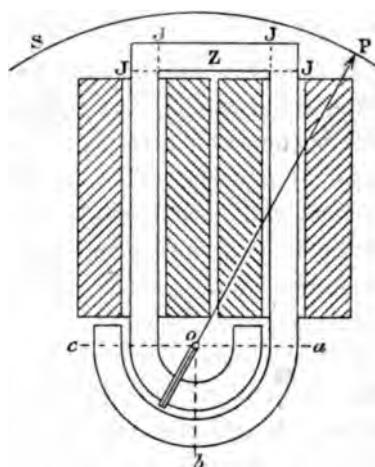


FIG. 5.

of its long sides as an axis (shown at O), the opposite side moving in the arc-shaped air gap between the poles. A pointer OP is attached to the coil and reads on a suitable scale PS. The magnetic joints, indicated at J, needed for constructional purposes, are made as good as possible by building up successive stampings, so as to overlap at the joints. The resistance of the magnetising coil (consisting of two windings, one on each limb) is reduced by using as much metal in the coil as the available winding space allows. Such constructional features ensure two desirable results. The ratio of the resistance of the coil to its impedance is made small, and the ratio of the magnetic leakage to the total magnetic flux is diminished as much as possible. The latter ratio cannot be assumed to be quite constant for different magnetising currents, so that, unless it is a small fraction, the

flux density at a particular part of the air gap may not always be sufficiently proportional to the total flux enclosed by the coil. The instruments actually made have been constructed to several designs, the earliest of which is indicated in fig. 4. In none of these instruments has any adverse effect due to variation of magnetic leakage been observed. But the instrument illustrated in fig. 4 is more likely to show such an effect than that illustrated in fig. 5. The magnet of fig. 4 consists of two blocks of stampings with butt joints at JJ, and measurement shows that while most of the magnetic flux through the centre limb crosses the narrow circular air gap in which the moving coil turns, an appreciable portion of the total flux leaks to the side limbs by longer air paths. In the magnet of fig. 5 this leakage must bear a much smaller ratio to the total flux.

The Inductance of the Moving Coil.

If the field coil of such an electromagnet be excited by an alternating voltage, and the moving coil be closed through a small resistance, this coil will be found to turn (in accordance with (16)) till the flux it encloses is as small as possible. Thus, in each of the cases represented in figs. 4 and 5, the coil will turn towards the position Oa. By increasing the resistance of the moving coil circuit the turning force can be easily made negligible, since, very approximately, the torque is inversely proportional to the square of this resistance (see (15)).

If the moving coil is connected with the terminals of a condenser and the field magnet coil be excited, the moving coil will be found to turn so as to enclose the greatest possible flux (see (18)). For the case represented by fig. 5 the coil will turn to the position Oc, while for that represented by fig. 4 the coil will turn to the nearer of the two positions Oc, Oc'.

These effects are quite in accordance with the theory previously given, but do not indicate any special facts about the self-inductance of the moving coil. More information is obtainable on this point by testing the formula (11)

$$T = C^2 \frac{dL}{d\theta},$$

where C is the moving coil current and L is the self-inductance of the coil. In order to test this formula, it is necessary to eliminate the torque, due to the interaction of the moving coil current, and the flux due to the current in the magnetising coil. This can be done by using currents of two different frequencies for the moving and field coils. Under these circumstances the only torque acting on the moving coil is that given by the above formula,

and by observing the movement of the coil we can thus find in which direction L increases.

Such tests were made upon an instrument constructed like fig. 5. The turning moment was found to be so minute that the controlling springs had to be removed, the current being passed into the moving coil by means of fine wires exerting no appreciable control. The moving system had also to be carefully balanced. The moving coil contained 20 turns, and the maximum current that could be safely passed through it was about 0.2 ampere. The magnetic force due to this current was feeble (the length of the magnetic circuit was about 15 inches, and the magneto-motive force was spent mostly on the gap), so that the permeability of the iron was low. The first test was made with the field magnet unexcited and with the field coil open circuited. An alternate current of 0.2 ampere through the coil caused it to turn to a position between Ob and Oc , about 30° from Ob as actually shown in fig. 5. The position of maximum self-inductance would, theoretically, be along Oc if the only magnetic circuit comprised the long iron path from pole to pole and the single air gap between the poles. The self-inductance is, however, partly due to the local magnetic circuit crossing the air gap twice, once on each side of the moving coil, and this portion of the self-inductance will be greatest when the coil lies along Ob . Hence, under the actual conditions, the position of maximum self-inductance must lie between Ob and Oc , as was indicated by the test. The field magnet coil (having 2000 turns and a resistance of 8.5 ohms) was then electrically closed, either by a short circuit, or by a small resistance, this latter consisting, in one case, of a single accumulator producing through the field coil a current of about a quarter of an ampere, and, in another case, of the low resistance armature of an excited alternator applied direct to the field coil. An alternate current of 0.2 ampere (produced by a second alternator) when passed through the moving coil caused the latter in each of these cases to turn to the position Ob . That is to say, whenever the field magnet coil was electrically closed (the total resistance of the circuit being in all cases small) the position of maximum self-induction of the moving coil was invariably Ob , whether the electromotive force impressed on the field magnet coil circuit was steady, alternating, or zero. Thus the self-inductance of the moving coil was dependent upon the resistance of the field coil circuit. To explain this, it must be remembered that a closed coil of low resistance has, approximately, the shielding effect of a perfectly conducting sheet. If we assume the resistance of the field coil to be zero, and the coil to be short circuited (or what is mathematically equivalent if a voltage be applied to it, the value of which is independent of current), it is theoretically impossible for the number of lines of force enclosed by the coil to be in

any way altered, unless there is an unbalanced electromotive force circuit, in which case the rate of change of the flux must be such as to produce a reactive electromotive force exactly balancing that which is impressed. In such case the closure of the field coil circuit would perfectly control the flux through the core, and this flux would be uninfluenced by the current in the neighbouring circuit such as that of the moving coil.

The theory of the instrument already given shows that it is necessary to carefully consider the inductance of the moving coil circuit. It is possible to construct the instruments so that this inductance has no appreciable influence on the deflections. Such a result may, at first, seem unlikely, but inductance, directly or indirectly, affects the deflection in three ways.

In the first place, the reactance causes a shift of phase of the moving coil current, and a resultant error similar to that which arises in a wattmeter of the ordinary dynamometer type.

Next there is the torque given by the formula

$$T_s = C^2 \frac{dL}{d\theta},$$

where C is the moving coil current, and θ is the deflection.

Finally, there is the torque due to inductive action given by (15) and

$$T_i = -\frac{1}{F} \frac{dF}{d\theta} LC^2 = -\rho \frac{d\rho}{d\theta} L \frac{V^2}{R^2}$$

and

$$\mathbf{F} = \rho \mathbf{N} \quad \text{or} \quad F\rho = \rho V,$$

where \mathbf{F} is the electromagnet flux, traversing the moving coil, the number of turns of which increases with the number of turns, and, therefore, with the inductance of this moving coil.

Moreover, it is necessary to consider whether the moving coil can be said to have a true, *i.e.*, constant, self-inductance, for the coil is always in the close neighbourhood of iron masses whose induction density, and, therefore, permeability, are continually varying throughout the period.

It must be borne in mind that the self-inductance of a coil is not a coefficient, convenient when constant, for connecting the magnetising current with the magnetic flux resulting from it, and that what is not associated with a magnetising current is not a magnetic flux but a magnetising force. The current causes no flux if the circumstances are such that the magnetising force due to the current merely calls into existence, by an equal and opposite magnetising force. The case is analogous to that of the weight of a body which causes no acceleration in it when at rest on a horizontal surface. If there is no extra flux due to the current in the coil, this coil

regarded as devoid of self-inductance. Such a result is, in the main, true of the coils of a potential transformer. The variation of the secondary current does not alter the flux through the core, since this flux is essentially controlled by the primary voltage; all that happens is a change in the primary current of such a character and amount as to exactly neutralise the change in the magnetising force due to the alteration of the secondary current. The flux through the core, as shown diagrammatically in fig. 6, consists of a

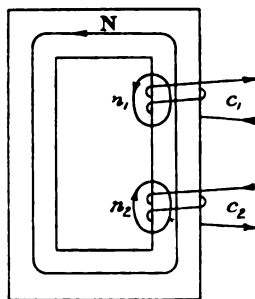


FIG. 6.

main portion N threading both the primary and secondary coils C_1 and C_2 , and traversing the best magnetic circuit, and also of two local, or leakage, fluxes n_1 and n_2 , each of which threads the windings of one coil only, and each of which traverses a bad magnetic circuit the reluctance of which is almost entirely due to that of an air path and, therefore, essentially constant. The flux N is determined by the primary voltage, and is independent of the currents in the coils C_1 and C_2 , but the flux n_1 is strictly proportional to the current in C_1 , while the flux n_2 is similarly proportional to the current in C_2 . If one of the coils, say C_2 , is on open circuit, the self-inductance of the other corresponds with a small flux n_1 strictly proportional to the current, together with a large flux N which, owing to the variable permeability of the iron, is not proportional to the current. Under these conditions the self-inductance is large but not constant. If, however, one of the coils, say C_1 , is excited by an alternating voltage, the self-inductance of the coil C_2 is solely due to the small flux n_2 . This leakage flux is proportional to the secondary current, so that energy is not dissipated when the flux alternates, and the coil has a constant self-inductance in spite of the presence of iron masses. But the inductance is very small, and it is possible that under some circumstances it may be actually less than would be the case if the iron masses were removed. The iron, with its voltage controlled flux N , diminishes the flux n_2 resulting from the current in the secondary coil, since it occupies paths otherwise available for this flux. For instance, if the primary coil C_1 is wound as in

fig. 5, so as to well cover the core, and the secondary consists of a few turns round the primary coil, the reluctance of the leakage path n_1 will, in such case, be so great that the secondary coil will be essentially devoid of self-inductance.

By those accustomed to transformers, and similar apparatus, it is recognised* that the self-inductance of the coil arises from the leakage flux, and not from the main flux; but I know of only one set of experimental tests in which the matter has been thoroughly investigated. These tests were carried out at King's College, London, in 1892, and are described in a report written by the late Dr. John Hopkinson for the Westinghouse Company.

The description in question is much more than an ordinary commercial report. It is a record of a searching experimental investigation on two transformers. Among the points examined was the instantaneous relationship of the leakage fluxes and the coil currents. Unfortunately this investigation has only been published in the technical press,† so that it may be useful to state briefly the experimental result of interest here.

Referring to fig. 6, if V_1 and V_2 are the voltages, A_1 and A_2 the currents, and r_1 and r_2 the resistances of the primary and the secondary coils respectively, we have

$$V_1 = r_1 A_1 + \dot{N} + \dot{n}_1,$$

with a similar equation for V_2 . The experiments showed that the leakage flux n_1 was proportional to the current A_1 for every instant of the period and for different magnitudes of the current A_1 . This was proved by determining the values and wave-forms of the different quantities required by means of Joubert's instantaneous contact method, using a quadrant electrometer as indicator. The curves for V_1 and $r_1 A_1$ were separately determined in the usual manner. The curve for \dot{N} was obtained with the aid of an open circuit coil surrounding the flux N , or by an equivalent method, and the curve for \dot{n}_1 was obtained from the others by using the above equation. The curve for A_1 was then differentiated to get the curve \dot{A}_1 , and the latter was finally compared with the curve for \dot{n}_1 . The two curves were found to coincide, and the comparison made was the more convincing because of the irregular and complicated shape of the curves. The tests were carried out

* As, for instance, in the much used "short-circuit" methods of testing alternate current machinery. The first of these short-circuit methods was pointed out by myself in 1892 in reference to the efficiency testing of transformers. See 'Proc. Inst. Elec. Engineers,' vol. 21, p. 741.

† See 'Electrician,' vol. 29, June 24 and July 1, 1892. I understand that most of the tests were actually carried out by Professor E. Wilson, who has since published in the 'Electrician' for February 15 and February 22, 1895, an account of some additional experiments which constitute further verification of some of the points here referred to.

not only with the secondary coil open circuited, but also with different load currents taken from this coil. The value of n_1 was found proportional to A_1 , and that of n_2 was found proportional to A_2 , at each instant, and under all circumstances, assuming constant voltage excitation of one of the coils.

It follows that the self-inductance of the moving coil is due to the part of the flux circulating through it, but not traversing the core surrounded by the field coil. In the case of fig. 5 the self-inductance will be greatest when the coil lies along Ob , and in that of fig. 4 the corresponding position will be Oa , but the self-inductance will be larger in the latter case owing to the leakage flux which passes through the moving coil, and traverses the closed iron magnetic circuit formed by the outer limbs of the magnet, without traversing the central core whose flux is controlled by the field coil circuit.

In several cases the impedance (and hence reactance) of the field coil was tested experimentally and found to compare satisfactorily with that calculated from the dimensions of the gap, the reluctance of the iron part of the magnetic circuit being negligible for the induction densities used in the tests. It was hence possible to deduce the reactance L_p of a field coil having the same number of turns as the moving coil. A quarter of this value will be the working reactance of the moving coil in the position Ob of fig. 5, since the two halves of the air gap will be in parallel for one magnetic circuit and in series for the other. It was thus possible to calculate the approximate value of the inductance of the moving coil for different values of θ , and to show that the values of L , and of $dL/d\theta$, were too small to affect the accuracy of the instruments actually constructed.

In some cases the value of L_p was measured directly. This was not a simple matter. It was necessary to use an alternate current method. It was useless to attempt to compare the impedance of the coil with its resistance, for these two quantities only differed by about one part in 5000, since the reactance was only about 2 per cent. of the resistance. A bridge method was actually used, the coil to be tested forming one arm, the other three consisting of non-inductive resistances, two of which measured about 1000 ohms each. All the resistances were suitable for, and were used with, currents of about 0.1 ampere. A pressure of 100 volts, alternating at a frequency of 50, was applied to the bridge. The cross conductor was arranged to have a resistance of about 200 ohms to reduce shunting errors, and contained an instrument capable of measuring pressures as low as 0.0002 volt applied to this conductor. So far as I am aware, no instrument for alternating currents is obtainable which is at all suitable for such a measurement. The voltage was measured after rectification by a suitable

commutator,* with the aid of a delicate galvanometer. To measure the minimum cross voltage it was necessary to make an extremely fine adjustment of the bridge. This was obtained by means of a sliding contact on a potentiometer wire 2 metres long and of about 9 ohms resistance. The minimum cross voltage, divided by the current through the coil under test, gave the reactance L_p of this coil.

An instrument of the type indicated in fig. 5 was examined by the above method. The moving coil contained 20 turns and had a resistance (including leads) of 11 ohms. It was fixed in the position O_b and its reactance was tested when the field coil was (i) on open circuit, and (ii) on short circuit. The values measured were respectively 0.160 and 0.136 ohm for a frequency of 50 cycles per second. The difference between these numbers is the part of the reactance due to the main magnetic circuit of the magnet, and its small value is attributable to the low permeability of the iron under the feeble magnetic forces due to the moving coil current. A coil of 15 turns, wound round the yoke of the magnet (at Z , in fig. 5), was also tested with currents of the same frequency. The resistance of this coil was 0.4 ohm, and its reactance was found to be 0.033 ohm with the field coil open circuited, and 0.014 ohm with the field coil short circuited. The two coils were afterwards put in series (opposing), and the reactance of the combination was found to be 0.147 ohm for the field coil short circuited, and 0.150 ohm for the field coil open circuited. The coils so connected were essentially non-inductive as regards their mutual magnetic circuit, so that the two above values should be equal to each other, and also to the sum of the numbers 0.136 and 0.014 found for the coils separately. This auxiliary coil was originally wound round the magnet for another purpose, being intended for use in series with the moving coil, and to be so connected that the voltages induced by the magnet in these coils opposed each other and balanced for a certain position of the moving coil. In this way the small error (see (15) and (33)) due to the voltage induced in the moving coil circuit could be eliminated or made negligible. The device was, however, found to be needless, owing to the insignificant amount of the error in question. A fixed auxiliary coil wound round the inner pole (near the line O_b in fig. 5) might in special cases prove useful, since essentially it would serve to remove from the circuit of the moving coil not only the voltage induced by the electromagnet, but also the self-inductance of the moving coil.

* For the commutator and voltmeter methods here referred to, see "The Measurement of Small Differences of Phase," 'Phil. Mag.,' January, 1905. They have been much used in connection with the present investigation for the determination of minute alternating voltages.

Measurement of Deflecting Torque.

The residual magnetism properties of an electromagnet such as is indicated in fig. 4 or fig. 5 are most striking, but the distribution of the magnetism in the air gap must be the same, whatever current may be passing through the field coil. All the instruments were calibrated by direct current methods. A steady current was passed through the field coil and maintained constant, while observations were made of the deflections in degrees due to various measured steady currents through the moving coil. The scale marking was made proportional to the current producing the corresponding deflection. The scale so obtained has been found in all cases accurate for alternate current use, being directly proportional for wattmeters, and proportional to the square of the volts for voltmeters. The air gap is bounded by two sets of stampings, those of each set having circular edges of the same radius, so that with good construction the air gap can be made very approximately of the same radial distance everywhere, and the wattmeter scale almost exactly equally divided. Tests have proved this to be the case.

For the purpose of verifying the formulæ given above for the torque T , acting on the moving coil, tests were also made of the voltage induced in this coil by the alternating electromagnet. For this purpose the alternating voltage on the magnet coil was kept constant, and the voltage of the moving coil measured for different values of the deflection θ . The ratio of the latter voltage to the former is ρ . The relation between ρ and θ was found in all cases to be very approximately linear. In the case of an instrument like fig. 5, ρ increased as θ altered from Oa to Oc , while, for an instrument like fig. 4, ρ passed through zero for some deflection denoted by Oa . The relation between ρ and θ was so nearly linear that it was found sufficiently accurate for the purpose of an approximate verification of the formulæ for T , to take as the value of $d\rho/d\theta$ the alteration in ρ for a change in θ of one radian, or $57^\circ.3$. The formulæ given are in absolute units, so that the unit torque is one erg per radian. It is convenient to measure the electrical quantities in commercial units, and the torque in "gramme centimetres," so that the formulæ for T , must be multiplied by $10^7/g$, or approximately by 10,200.

One instrument tested had a field coil of 990 turns. The moving coil contained 20 turns, and its working range was 140° . This coil was fixed at deflections of 0° , 20° , 40° , 60° , 80° , 100° , 120° , and 130° , and the measured values of ρ expressed as percentages were respectively 0.38, 0.50, 0.64, 0.77, 0.91, 1.05, 1.18, and 1.23. These values will be found to plot very well on a straight line, the slope of which corresponds with a rate of 0.39 per cent. per radian.

Using σ for shortness to denote $10,200 \, d\phi/d\theta$, the above tests imply that σ is 39.8. Formulæ (28), (29), and (30) for T , expressed in gramme-centimetres become respectively

$$(i) \, \sigma \overline{CN}; \quad (ii) \, \sigma KV^2; \quad (iii) \, \sigma \frac{M}{R} W.$$

The strength of the spring was first tested mechanically by placing a wire rider, weighing about 20 milligrammes, on the pointer at a measured distance from the axis, and carefully adjusting the instrument till the pointer and the axis were each horizontal, first with and then without, the rider. In this way the torque for 80° deflection was measured as 0.126 gr. cm., corresponding with 0.142 gr. cm. for 90° . The instrument was then tested as a voltmeter with a standard condenser of 0.5 microfarad for the moving coil circuit. A number of tests made for deflections near 80° yielded as a mean result that 79 volts produced a deflection of 81° . Substituting in the formula $\sigma = 39.8$; $K = 0.5 \times 10^{-6}$; $V = 79$, we get 0.124 gr. cm. for 81° , or 0.138 gr. cm. for 90° . A test on the instrument as a wattmeter on a non-inductive load, measuring the current and voltage with hot wire instruments, resulted in a deflection of 126° for 94 volts and 18 amperes, or for 1692 watts, when the transformer was such that M was approximately 0.305 millihenry, and R , the total resistance of the moving coil circuit, was 108.8 ohm. These numbers, when substituted in the above formula, give 0.189 gr. cm. for 126° , or 0.135 gr. cm. for 90° . Thus the mechanical tests and those using formulæ (ii) and (iii) yield values respectively 0.142, 0.138, and 0.135 gr. cm. for a deflection of 90° .

This instrument was afterwards altered. A moving coil of 44 turns replaced the original one of 20 turns and stronger controlling springs were used, the torque for 90° measuring approximately 1.10 gr. cm. The value of σ was not again measured, but it may be assumed to increase in proportion to the number of turns on the moving coil, and hence may be taken as $39.8 \times 44/20$, or 87.6. Two transformers were successively used with this instrument, the resistance of the moving coil circuit being adjusted in each case till the instrument gave a deflection of exactly 50° for 1000 watts. The values of M for the two transformers were measured approximately as 0.765 and 1.00 millihenry. The corresponding resistances for the moving coil circuit were 114.1 and 150.6 ohms. On substituting in formula (iii) above the two values of the torque for 50° work out to be 0.587 and 0.582 gr. cm., or, for 90° , 1.056 and 1.047 gr. cm. When used as a voltmeter with a condenser of 1.43 mf., the instrument gave a deflection of 95° for a pressure of 97 volts. On substituting in formula (ii) these numbers will be found to correspond with a torque of 1.12 gr. cm. for 90° .

A test was also made using formula (i) in connection with an instrument referred to in subsequent tests (see Table II). It was found that when 107 volts at a frequency of 52 were applied to the fixed coil and moving coil in series, the resultant deflection was 58° . The value of σ found for this instrument was approximately 56, and the torque required to deflect the spring 90° was 1.24 gr. cm. The field coil was such as to take 90 milliamperes for a voltage of 200 when the frequency was 50 cycles per second, hence for 107 volts and 52 cycles per second the value of C in (i) is 0.0463 ampere. The value of N is such that $2\pi \times 52N = 107$, or N is 0.328. Hence, σCN is 0.848 gr. cm. for 58° , or 1.32 gr. cm. for 90° . This result would have been nearer 1.24, the value found from the mechanical test, if allowance had been made for the phase difference ϕ_i between the magnetising current C , and the resultant flux N . The angle ϕ_i , judging from measurements made on other instruments, is about 13° , and though large enough to be fatal for a wattmeter having an electromagnet of the ordinary series, or current controlled type, is not such as to make $\cos \phi_i$ differ more than 3 or 4 per cent. from unity.

No attempt was made to prove exact coincidence between the mechanically and electrically measured values of the torque. The tests in question really constituted absolute measurements, and in order to carry them out properly it would have been necessary to most carefully check all the instruments, and subsidiary measurements, made use of. This was not done, since only an approximate verification was aimed at. Many such tests were made on the various instruments constructed. The results above given are taken from the more concordant tests. The indications of the commercial instruments used were accepted without verification.

Condenser Compensation.

The most serious error arising in the action of the wattmeter on circuits of low frequency and low power factor is that due to the resistance of the field coil. The self-inductance of the moving coil circuit tends to increase the effect of this error, not to compensate it. The voltage V applied to the field coil of resistance r produces a current A_m which magnetises the core and causes a reactive voltage U or \dot{N} . These quantities are related by the equation

$$V = rA_m + U,$$

and in fig. 7 are represented respectively by the vectors BP, BO, and OP. If the number of turns on the field coil is m the product mA_m can be represented to some other scale by BA drawn along BO, and is the number of ampere turns round the core needed to magnetise it to the extent represented by the

reactive voltage U . The error of the instrument arises from the phase difference between U and V , not from the fact that the magnitude of U is less than that of V . The ratio between U and V is independent of the current and the power factor, and is essentially the same for all voltages. In all cases it differs inappreciably from unity, and any difference that exists is taken account of in the standardisation of the instrument.

For a given frequency the relationship between the total magnetising ampere turns BA round the core, and the reactive core voltage OP is quite fixed by the magnetic circuit, even if there are several coils round the core traversed by independent currents. Suppose that in addition to the primary

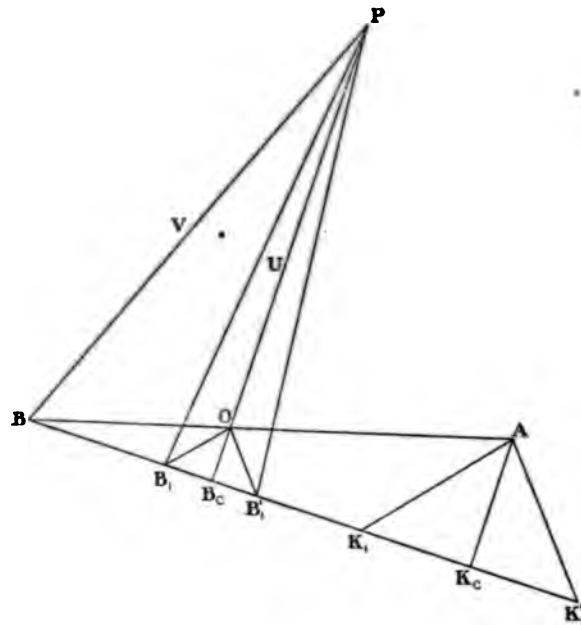


FIG. 7.

exciting coil already referred to there is a second winding of m_2 turns round the core, and that the terminals of this coil are joined to a condenser. The voltage V_1 on the primary necessary to produce a reactive voltage U due to the core, will now be given by

$$V_1 = rA_1 + U,$$

where A_1 is the new current in the primary. Since mA_m is the total number of ampere turns necessary to produce the core voltage U , we have

$$mA_1 + m_2A_2 = mA_m,$$

where A_2 is the condenser current. The current A_2 will necessarily be in quadrature with the core voltage U , since it is in phase with \dot{U} , and hence

$m_2\mathbf{A}_2$ will be represented by a vector \mathbf{BK}_1 , perpendicular to \mathbf{OP} , while its magnitude will be proportional to the capacity of the condenser applied to the secondary winding. Since the vectors \mathbf{BA} and \mathbf{BK}_1 represent respectively $m\mathbf{A}_m$ and $m_2\mathbf{A}_2$, it follows that $\mathbf{K}_1\mathbf{A}$ will represent $m\mathbf{A}_1$ and that if \mathbf{OB}_1 be drawn parallel to \mathbf{AK}_1 to meet \mathbf{BK}_1 in \mathbf{B}_1 this vector will denote $r\mathbf{A}_1$, while the vector $\mathbf{B}_1\mathbf{P}$ will represent \mathbf{V}_1 . By increasing the capacity of the condenser attached to the secondary winding, the point \mathbf{B}_1 may be made to reach the line \mathbf{OP} at \mathbf{B}_c and even to cross it to \mathbf{B}_1' , so that the phase difference between \mathbf{V}_1 and \mathbf{U} can be reduced to zero and can even be reversed in sign until from an angle of "lag" it becomes an angle of "lead." It is thus possible by the use of a condenser of the right capacity to compensate not only the phase error of the electromagnet, but also the extra phase error due to the inductance of the moving coil circuit. The adjustment will hold for different voltages, but will only be exact for one frequency. This is all that is needed in most cases, since one of the most constant properties of an alternate current system of distribution is its frequency.

In the case considered the length of the line \mathbf{OP} is from 100 to 200 times the length of \mathbf{OB} , so that to a close approximation the lines \mathbf{BP} , $\mathbf{B}_1\mathbf{P}$, \mathbf{OP} , etc., are all of equal length. Also the angle \mathbf{BOP} does not much exceed a right angle, and hence \mathbf{BA} and \mathbf{BK}_c are essentially equal. The angle \mathbf{OBB}_c is about 13° , while the angle \mathbf{BPO} is only about a quarter of a degree. If the field coil of the electromagnet be excited at constant voltage and frequency, the reactive voltage \mathbf{U} can thus be regarded as fixed, whatever the capacity \mathbf{K} of the condenser applied to the secondary winding. For a zero value of \mathbf{K} the primary current will have a certain value represented by \mathbf{BA} . For a particular value \mathbf{K}_c of the capacity, the primary current will be a minimum represented by \mathbf{AK}_c , the line \mathbf{BK}_c representing to some other scale the capacity \mathbf{K}_c . For any other capacity \mathbf{K}_1 , represented by \mathbf{BK}_1 , the corresponding primary current will be represented by \mathbf{AK}_1 . Thus, if the magnet be excited at constant voltage and frequency, and measurements of the primary current be taken for various values of \mathbf{K} , the curve obtained by plotting the primary current or ampere turns as ordinates, and the corresponding values of \mathbf{K} as abscissæ, will be catenary-shaped with a minimum ordinate for the capacity \mathbf{K}_c needed to compensate the phase error of the magnet. Such curves are well known in connection with alternate current measurements. When suitable scales are chosen the curve must also be such that the ordinate is equal to \mathbf{AK}_1 when the abscissa is equal to \mathbf{BK}_1 in fig. 7. The value of \mathbf{K}_c obtained will be inversely proportional to the square of the current frequency used, since the ampere turns \mathbf{BA} needed to produce a given reactive voltage \mathbf{U} will vary inversely as the frequency, while the ampere

turns BK_1 due to a capacity K_1 will be directly proportional to the frequency. For a similar reason the capacity needed will be inversely proportional to the square of the number of turns used on the secondary winding. All these points have been fully verified by actual tests.

The results given below in Table I and fig. 9 are taken from a set of tests made on an electromagnet provided with a moving coil, and connected up as a voltmeter of the magnetostatic type previously described. The connections of the coils are shown diagrammatically in fig. 8. The field coil

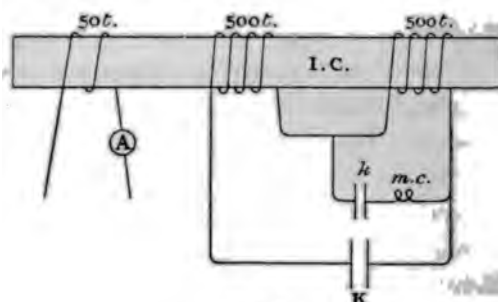


FIG. 8.

consisted of two coils of 500 turns each, the two coils being twin wound round the core so as to ensure that each coil enclosed the same flux. These coils were permanently connected in series. The moving coil, *m.c.*, was connected to the terminals of one of the windings of 500 turns through a condenser *k* of 0.5 microfarad capacity. The core of the magnet was wound with an extra coil of 50 turns. The pointer was found to deflect to a certain mark on the scale when 80 volts were applied to 1000 turns (or 40 volts to 500 turns). The deflection for a given voltage was the same for any ordinary frequency of the voltage used for the test. This deflection was utilised in the tests to adjust the reactive voltage of the core to a constant value. Experiments were then made by passing an alternating current of *A* amperes through the 50-turn coil. The current frequency was kept constant at 80 cycles per second, and *A* was adjusted by means of suitable resistances until the pointer was steady at the mark on the scale, the current being read by a hot wire ammeter. The values found for *A* for different capacities of *K* microfarads applied to the field coil of 1000 turns are given in the first two columns of Table I. A third column gives the corresponding values of 50*A* or the ampere turns associated with the 50-turn coil. The value of *K* was known with fair accuracy, and was due to various parallel combinations of condensers which had been tested by ballistic methods some months previously. The half microfarad condenser used with the

1000-turn coil for the moving coil circuit caused a small magnetising current in the field windings. The values given for K represent the capacities usually connected with the 1000-turn coil, and these should be each increased by 0.5/4 or 0.125 microfarad to get numbers proportional to the ampere turns due to the condenser currents.

Table I.

| A. amperes. | K. mf. | 50A. amp. turns. | A. amperes. | K. mf. | 50A. amp. turns. |
|----------------|-----------|---------------------|----------------|-----------|---------------------|
| 3.1 | 0.0 | 155.0 | 0.70 | 4.33 | 35.0 |
| 2.16 | 1.58 | 108.0 | 0.85 | 5.02 | 42.5 |
| 2.2 | 1.62 | 110.0 | 1.0 | 5.35 | 50.0 |
| 1.83 | 2.0 | 91.5 | 1.70 | 6.64 | 85.0 |
| 1.69 | 2.33 | 84.5 | 1.87 | 6.93 | 93.5 |
| 1.28 | 3.02 | 64.0 | 2.79 | 8.55 | 139.5 |
| 0.95 | 3.58 | 47.5 | 3.23 | 8.97 | 161.5 |
| 0.93 | 3.62 | 46.5 | | | |

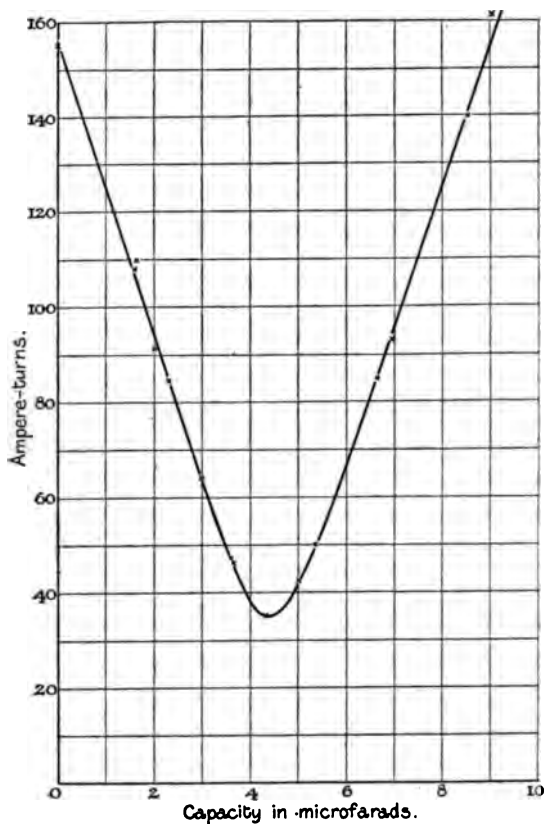


FIG. 9.

The results are shown plotted in fig. 9. When the current A has its minimum value, reference to fig. 7 will show that A is in phase with the reactive voltage. Hence the power wasted in the core may be obtained by multiplying the minimum number of ampere turns, 35, by 0.080 the voltage per turn round the core. This power works out to be 2.8 watts for 80-cycle circuits for the induction density corresponding with this frequency and 0.080 volt per turn. The loss thus obtained agrees closely with other measurements which have been made upon the core losses of the electro-magnet in question.

A more convenient method of testing one of these instruments for the capacity K_c needed for compensation is (see fig. 10) simply to put the field coil $f.c.$ in series with the moving coil $m.c.$ and to apply various condensers K to the terminals of the field coil only, when a constant voltage V is applied to the two coils in series, the frequency being kept constant. The impedance of the moving coil is quite negligible compared with that of the field coil. Hence for constant voltage and frequency the reactive voltage U (fig. 7) is constant. The magnetic field, which is in quadrature with U ,

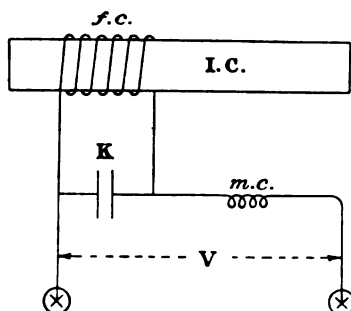


FIG. 10.

is represented by a vector drawn along the line BK and is fixed both in phase and magnitude. The vector BA represents the field coil current, which in this case includes the condenser current, but the moving coil current is represented by AK , for a capacity K , applied to the field coil. Since the magnet field is represented by a vector of constant length drawn along BK , the torque acting on the moving coil will be represented by the projection of AK_1 on BK_c or by K_1K_c . It will thus reverse in sign as the capacity increases through K_c , the value needed for compensation, and, moreover, there will be a linear connection between the capacity used and the moving coil torque as indicated by the deflection on the calibrated wattmeter scale.

The results given in Table II, and shown plotted in fig. 11, illustrate one of many tests made on a number of instruments by this method.

Table II.

| | | | | | | | |
|----------|----|------|------|------|-------|-------|-------|
| K | 0 | 0.50 | 1.00 | 1.48 | 1.96 | 2.46 | 2.96 |
| θ | 58 | 36.5 | 13.5 | -1.0 | -23.8 | -48.0 | -68.0 |

The voltage was kept constant at 107 volts and the frequency was always adjusted approximately to 52 cycles per second, by means of a resonance frequency meter. K is the capacity in microfarads shunted to the field magnet coil, and θ is the deflection of the instrument. The negative

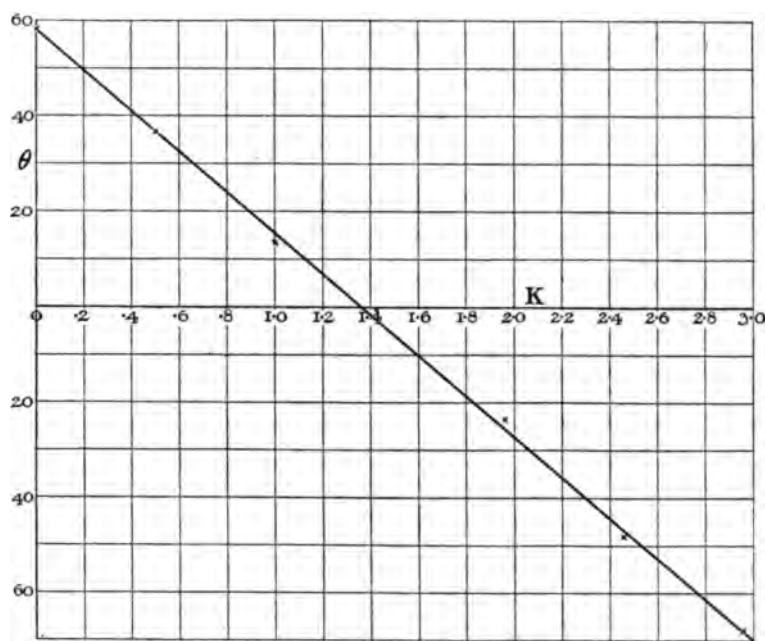


FIG. 11.

readings were obtained by reversing the connections of the moving coil. The instrument was the same as that referred to later in the tests on compensated wattmeters, the field winding consisting of four coils in parallel, each coil containing 2000 turns. From the plotted results it appears that K_c is 1.37 microfarads for a frequency of 52, corresponding with $1.37 \times (52)^2 / (50)^2$, 1.48 microfarads for circuits of frequency 50. The ampere turns due to the condenser winding if the frequency is 50, the voltage is 200, and $K = 1.48$ mf. will be $2000 \times 1.48 \times 10^{-6} \times 314 \times 200 = 186$. This is approximately the value of mA_m for this frequency and voltage, since tests showed that for 200 volts at 50 cycles per second the value of A_1 was

90 milliamperes, corresponding with 180 ampere turns. The agreement is satisfactory in view of the fact that the frequency was not adjusted with any special care.

Compensated Wattmeters.

The foregoing theory shows that a wattmeter of the type here considered, if correctly calibrated on non-inductive loads, will, when used on inductive loads, of power factor $\cos \phi$, give a reading denoting

$$W [1 - \phi_e \tan \phi],$$

where W is the true power in watts, and ϕ_e is the phase error of the instrument given by (36). The wattmeter reads low for lagging currents, and high for leading currents in direct contrast to the behaviour of a wattmeter of the ordinary dynamometer type.

When an additional coil is wound round the core and connected to the terminals of a condenser, the value of ϕ_e is given by the formula

$$\phi_e = \phi_m + \phi_c + \phi_i - \phi_o,$$

where ϕ_c is the phase angle corresponding with the condenser winding and which is proportional to the capacity of the condenser attached to this winding. The ratio of ϕ_c to ϕ_m will approximately be that of the ampere turns due to the condenser to the ampere turns needed to magnetise the core.

By using a suitable condenser it is possible to reduce ϕ_e to zero and even to reverse its sign, that is to make the wattmeter read high for lagging currents and low for leading currents, like an ordinary dynamometer wattmeter. This has been experimentally verified on several wattmeters the electromagnets of which differed greatly in shape. The following results were obtained on a wattmeter having an electromagnet shaped like that represented in fig. 5. This instrument had been wound for use as a multirange voltmeter. The magnet was wound with four coils each of 2000 turns. Two of these coils were wound on each limb, one coil being completely wound on the bobbin before the winding of the other was commenced. The resistances of the four coils are 74.5, 93.0, 71.5, and 90.4 ohms, the two lower resistances corresponding with the inner coils, and the others with the outer coils. With all four coils in parallel it was found that 200 volts produced a current of 0.090 ampere when the current frequency was 50, so that 180 ampere turns were needed to produce a flux density in the core corresponding with 10 turns per volt at 50 cycles per second, and it follows that the impedance of the winding is 2222 ohms at this frequency. The parallel resistance of all four coils is 20.3 ohms. The two inner coils when in parallel measure 36.5 ohms and the two outer coils

in parallel measure 45.9 ohms. Hence the value of ϕ_m , or the ratio of resistance to impedance, is as given in Table III for different combinations of coils and for frequencies of 50 and 80.

Table III.—Values of ϕ_m .

| Frequency. | 50. | 80. |
|----------------------------|-----------|-----------|
| | Per cent. | Per cent. |
| All coils in parallel..... | 0.92 | 0.57 |
| Inner " " | 1.65 | 1.03 |
| Outer " " | 2.07 | 1.29 |

The above values are higher than those obtained in other instruments of the same type, the reason being that the winding consisted of a large number of turns of thin wire insulated for high potential working, so that the space occupied by the insulation was unusually large compared with the space occupied by the copper.

The moving coil was connected up in series with the secondary of a current transformer, and a non-inductive resistance, the total resistance of the circuit being 118 ohms. The transformer had a primary and secondary coil each of 94 turns, the former being suitable for current up to 10 or 15 amperes, and the latter consisting of fine wire. The reactance Lp of the secondary was 0.24 ohm at 50 cycles per second. The mutual inductance of the coils was 0.765 millihenry. The value of ϕ_s due to the reactance of the secondary was $0.24/118$, or 0.203 per cent. at 50 frequency, corresponding with 0.325 per cent. at 80 frequency. The transformer actually used contained iron (and an air gap) in its magnetic circuit, so that the value of ϕ_s must be allowed for. Measurements* showed that its value varied from 0.3 to 0.4 per cent. in accordance with the currents used.

If for the moment the self-inductance of the moving coil itself be neglected it will be seen that for a frequency of 80, and using all four coils

* Owing to the length of the present paper, no reference is made to the conditions for accuracy of a quadrature transformer containing iron in its core, but the tests made in this connection have been most numerous. To measure ϕ_s an air core transformer was chosen, the coils of which had about the same mutual inductance as those of the iron core transformer to be tested; an alternating current was passed through the two primaries in series, and measurements were made of the phase difference of the two secondary voltages. This was done by means of the voltmeter methods already referred to, taking due care to allow for the phase differences introduced by the self-inductance of the secondary coils. The testing networks used were essentially either Felici or Christie balances, and in some cases the phase difference measured was increased, and in others diminished, by the self-inductance of the secondaries.

in parallel for the field coil, the values of ϕ_m , ϕ_s , and ϕ_i are respectively 0.57, 0.32, and 0.35 per cent. The sum of these numbers is 1.24 per cent. If the field coil consists only of the two outer coils in parallel, this number, owing to the increase of ϕ_m , becomes 1.96 per cent. Tests of the uncompensated wattmeter on circuits of frequency 80 and for loads of power factor $\cos \phi$, have shown percentage errors given by the formula

$$\phi_s \tan \phi$$

for values of ϕ_s in close agreement with the above numbers.

An approximate value of the reactance of the moving coil can be obtained from the impedance of the 2000 turns of the field winding. This, for a frequency of 50, is 2222 ohms. The moving coil consisted of 40 turns. If the field coil contained only 40 turns, the impedance would be $2222 \times (40)^2 / (2000)^2$, or 0.89 ohm. The moving coil, when in the central part of the gap, will have its reactance a maximum, and approximately equal to a quarter of the above value. It will thus be 0.22 ohm for a frequency of 50, or 0.35 ohm for a frequency of 80. Since the resistance of the moving-coil circuit is 118 ohms, the phase error due to the coil's reactance will be 0.3 per cent. for 80 cycle circuits, and this will be its maximum value. As already stated, the total phase error ϕ_s is the vector sum, and is less than the numerical sum, of the different phase errors. I have generally found that the value of ϕ_s , experimentally deduced from tests of the wattmeter on inductive loads, agrees well with that calculated from adding the separate phase errors, when that due to the reactance of the moving coil is neglected.

In order to test the iron-cored instrument (I.C.W.) as a compensated wattmeter, the outer coils were put in parallel, and used as the field winding, to which the voltage was applied, while the inner coils, also in parallel, were applied to the terminals of a condenser. The tests were made, using as a standard wattmeter a Mather Duddell instrument (M.D.W.), constructed by Messrs. Paul. In order that the tests on lagging current loads could be immediately succeeded by tests on leading current loads, and *vice versa*, the circuits were arranged as shown in fig. 12.

Two similar single-phase alternators, rigidly coupled so as to run together, generated two voltages \mathbf{V}_1 and \mathbf{V}_2 of the same frequency and approximately in quadrature. The magnitudes of \mathbf{V}_1 and \mathbf{V}_2 could be varied independently by adjusting the exciting currents of the two machines. The current \mathbf{A} was produced by the voltage \mathbf{V}_1 , and passed through (i) the primary P of the current transformer of the I.C.W.; (ii) the current coils C of the M.D.W.; (iii) a large non-inductive resistance R consisting of glow lamps; and (iv) a small adjustable carbon resistance CR. This current was approximately in

phase with the voltage V_1 , but there was a slight angle of lag owing to the inductance of the coils in the circuit. The voltage V for the pressure coils of the two wattmeters was obtained from the mains M , N , which were connected up to the two alternators with the aid of a reversing switch, $R.S.$, so arranged that, for one position of the switch, $V = V_1 + V_2$, and for the other position, $V = V_1 - V_2$. The vector figure is indicated in fig. 13. The current A was in each case approximately 45° out of phase with the voltage V , leading for one position of the switch ($V = V_1 - V_2$) and lagging for the other position ($V = V_1 + V_2$). Its magnitude in the various tests varied from 7 to 9 amperes, being in all cases adjusted by the carbon resistance $C.R.$ till the M.D.W. was balanced. The voltage V for one position of the switch was about 230 volts, and for the other about 200 volts. The frequency was in all cases adjusted to 80 cycles per second. The pressure circuit of the

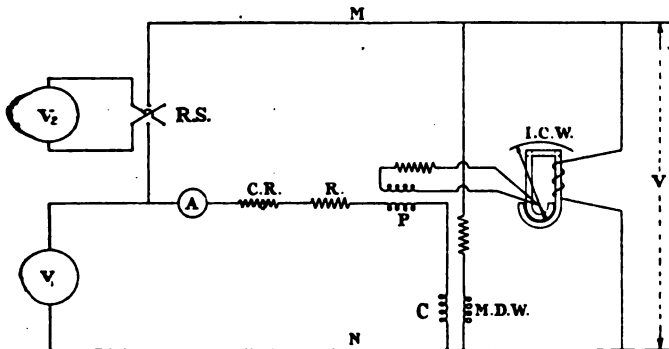


FIG. 12.

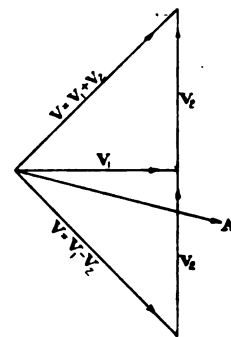


FIG. 13.

M.D.W. contained a non-inductive resistance of 9000 ohms, which was amply sufficient to make this circuit essentially non-inductive for a frequency of 80. One terminal of this resistance was connected to the main M , so that the pressure coil of the M.D.W. had one of its ends joined directly to the main N , and was thus at essentially the same potential as the current coil C . This precaution was found necessary to make negligible any electrostatic forces acting on the moving system of the M.D.W., this moving system being large and delicately suspended. The constant of the M.D.W. had been carefully determined on a non-inductive load, using the same hot wire instruments to measure the pressure and current as were afterwards employed to measure the same quantities for the inductive tests. The power factor $\cos \phi$ of the load was determined in each case from the readings of the volts, amperes, and of the watts, as indicated by the hot wire instruments and the M.D.W. From the power factor $\cos \phi$ the value of $\tan \phi$ was deduced, this value

being considered positive for lagging currents ($V = V_1 + V_2$) and negative for leading ones ($V = V_1 - V_2$).

In Table IV, below, the first column shows the capacity in microfarads joined up to the two parallel connected inner coils wound round the electromagnet core. The reduced readings of the M.D.W. for a deflection of exactly 40° on the I.C.W. are next given, arranged in three columns, in order to separate the results obtained with the three kinds of load corresponding with the voltage used. The last two columns show the value of the power factor as deduced from the readings of voltmeter, ammeter, and wattmeter, and the corresponding value of $\tan \phi$.

Table IV.

| Capacity K. | Readings of M.D.W. | | | $\cos \phi$. | $\tan \phi$. |
|----------------|--------------------|-----------|-----------------|---------------|---------------|
| | $V = V_1 + V_2$ | $V = V_1$ | $V = V_1 - V_2$ | | |
| 0 | — | — | 63.0 | 0.852 | -0.613 |
| | — | 63.4 | — | 1.000 | 0 |
| | 64.6 | — | — | 0.755 | 0.869 |
| | — | — | 62.9 | 0.796 | -0.758 |
| | 65.0 | — | — | 0.799 | 0.753 |
| | — | — | 62.4 | 0.796 | -0.758 |
| 2.0 | 64.6 | — | — | 0.799 | 0.753 |
| | 62.0 | — | — | 0.748 | 0.884 |
| | — | 63.4 | — | 0.994 | 0.100 |
| | 62.5 | — | — | 0.755 | 0.815 |
| | — | — | 64.8 | 0.823 | -0.688 |
| | 62.7 | — | — | 0.748 | 0.884 |
| 0.9 | — | — | 64.8 | 0.823 | -0.688 |
| | 63.6 | — | — | 0.748 | 0.884 |
| | — | 63.6 | — | 1.000 | 0.000 |
| | — | — | 63.6 | 0.822 | -0.688 |

The results show that (i) the uncompensated instrument ($K = 0$) is more sensitive for lagging currents than for lagging ones; (ii) when a capacity of 2 microfarads is used the reverse is the case; and that (iii) when a capacity of 0.9 microfarad is used, the instrument is perfectly compensated for circuits of frequency 80. It was easy to test the effect on the reading due to suddenly switching on the condenser K, and there was no doubt that for lagging currents switching on the condenser caused an increase of the deflection of the I.C.W., while for leading currents the reverse effect took place. When the load was essentially non-inductive no effect due to switching on a condenser could be observed. This is only natural, since

when $\phi = 0$ the error $\phi_e \tan \phi$ vanishes, whatever the value of ϕ_e . But though the nature of the effect due to the condenser current could thus be easily demonstrated, it needed a set of tests such as those indicated in Table IV to actually measure its amount. The numbers given are in each case the means of several observations, and only a few of the tests taken are given. This more especially applies to the observation with $K = 0.9$ microfarad. These were repeated many times, with the result that it was impossible to say under the actual conditions of test whether the I.C.W. was more, or was less, sensitive with load currents lagging than with load currents leading. It now only remains to show that the differences actually observed are in accordance with the error formula.

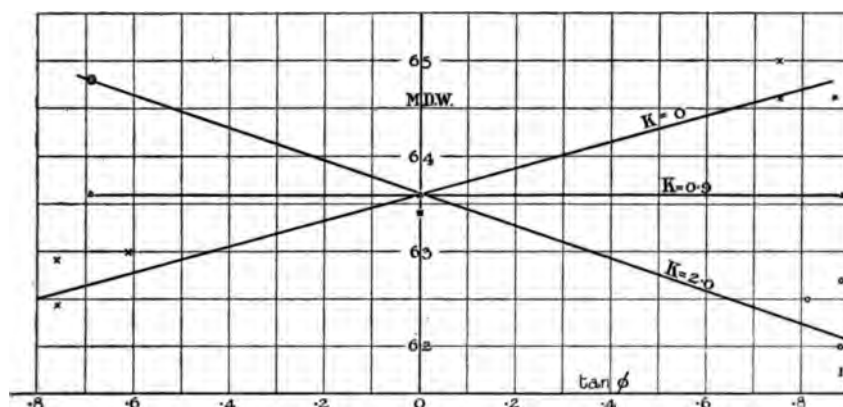


FIG. 14.

The results given in Table IV are plotted in fig. 14, abscissæ representing values of $\tan \phi$ and ordinates the corresponding wattmeter readings for the standard deflection of the I.C.W. These results are found to plot fairly closely on three straight lines, each having the ordinate 63.6 for the zero value of $\tan \phi$. The resultant phase errors calculated from the slopes of the lines in fig. 15 will be found to be 2.05, 2.68, and 0 per cent. for values of K respectively, equal to 0, 2, and 0.9 microfarads. Owing to the nature of the error formula $\phi_e \tan \phi$, the mean value of ϕ_e can be best obtained numerically by taking the mean wattmeter reading and the corresponding mean value of $\tan \phi$ for each set of tests, and combining the results as indicated in Table V.

R denotes the ratio of the difference between the wattmeter readings to the corresponding difference between the tangents, while the ratio of R to 63.6 is ϕ_e , the phase error.

Now, as already shown, the calculated values of ϕ_m , ϕ_e , and ϕ_i add up to

Table V.

| K. | Wattmeter readings. | | tan ϕ . | | Differences in— | | R (ratio). | ϕ_c (per cent.). |
|-----|---------------------|-------|--------------|---------|-----------------|--------------|------------|-----------------------|
| | Lag. | Lead. | Lag. + | Lead. — | Reading. | tan ϕ . | | |
| 0 | 64.73 | 62.77 | 0.784 | 0.710 | 1.96 | 1.494 | +1.31 | +2.06 |
| 2.0 | 62.40 | 64.80 | 0.750 | 0.688 | -2.40 | 1.438 | -1.67 | -2.62 |
| 0.9 | 63.60 | 63.60 | 0.884 | 0.688 | 0 | 1.572 | 0 | 0 |

1.96 per cent., disregarding the self-inductance of the moving coil, which will increase the number by an amount less than 0.3 per cent. This figure agrees closely with the phase error of 2.06 per cent. as actually measured for $K = 0$. The value of ϕ_m or the shift in the value of ϕ_c , caused by applying condensers of 0.9 and 2 microfarads to the secondary winding, will be seen from the tests to be 2.06 per cent. and 4.68 per cent. respectively. These numbers can readily be compared with the values calculable from the capacities. The value of ϕ_m alone, as shown by Table III, is 1.29 per cent. for an exciting winding consisting of the two outer coils in parallel and for the frequency of 80. Also, it was found that 180 ampere turns round the field winding produced a magnetic flux corresponding with 0.1 volt per turn at a frequency of 50, and, therefore, with 0.16 volt per turn at a frequency of 80. The alternation of such a flux would induce in 2000 turns a pressure of 320 volts at the latter frequency. Assuming the wave form of the voltage approximately sinuous, as was the case in the actual tests, a condenser of 1 microfarad applied to the 2000 turns under the conditions assumed would take a current of $2\pi \times 80 \times 10^{-6} \times 320$ ampere, or 0.161 ampere, corresponding with 332 ampere turns for the coil of 2000 turns. The value of ϕ_c for a condenser of 1 microfarad is, therefore, very approximately given by

$$\frac{322}{180} 1.29 \text{ per cent.} = 2.32 \text{ per cent.}$$

Hence, condensers of 0.9 and 2 microfarads would, at the frequency of 80 assumed, produce values of ϕ_c respectively equal to 2.09 per cent. and 4.64 per cent., which are essentially the same as the values actually found. The testing conditions were such that the closeness of the agreement is of no special significance, but it will be apparent that within the limits of experimental error the action of the wattmeter corresponds exactly with the formula given for it.

Conclusion.

The foregoing tests were all made with alternate currents of the low frequencies usual in commerce, on instruments of the non-reflecting type, each having a moving system subject to the control of a strong spring. Few tests have yet been made on reflecting instruments in which a weak control is used for the moving coil. Under such conditions much greater sensitiveness can naturally be secured, but, owing to causes already mentioned, the sensitiveness reached will not even then be comparable with that obtainable with the best direct current galvanometers. To measure very minute alternate currents or voltages it must ultimately prove necessary to use instruments of the heterostatic type. For such purposes the shunt-excited electromagnet seems specially suited, and additional interest in consequence attaches to the foregoing examination of the behaviour of voltage-controlled magnetic fields.

The precision of direct current measurements is mainly due to the use of null methods. Analogous methods have been suggested, or can easily be devised, for alternate current testing. But such methods are not used. The advantage of a null method arises from the possibility of fully utilising the sensitiveness of an instrument for the purpose of measuring or indicating a small difference between two nearly equal quantities. It follows that when, as with alternate currents, instruments sufficiently sensitive to indicate such a difference do not exist, null methods are really of little value. In fact, when the testing voltmeter is such that the deflection depends on the square of the voltage, a direct deflection method is more sensitive than a balance method, assuming the voltage tested is not large enough to over-deflect the instrument. By making use of the properties of separately excited voltage-controlled fields it seems possible to construct voltmeters for alternate current working which are quite as sensitive as the corresponding direct current instruments, and which are also such that the deflecting forces are proportional to the first power of the voltage tested. The special difficulties due to phase can be readily overcome, since it is easy to apply in succession to the field coil two voltages of known relative magnitude and phase. For the purpose of null methods the magnitudes of these voltages need only be very roughly determined.

The instruments yet made have been suitable only for low-frequency circuits. For high-frequency working special difficulties will arise, while others will disappear. For low frequencies the chief difficulty is to make negligible the phase error ϕ_m , represented approximately by the ratio of resistance to impedance. For high frequencies ϕ_m will become quite

negligible, but on the other hand ϕ_s , the phase error due to the inductance of the moving coil circuit, will become serious, as also possibly will eddy current effects in the core of the electromagnet. Eddy currents in the core only affect the accuracy of the magnet in so far as they affect the value of ϕ_m , provided the core is so well laminated that the distribution of the magnetic field is the same for direct as for alternate currents. With very high frequency currents the value of ϕ_m will be negligible, and, possibly, in some cases, there will be no need to use iron in the core, so that eddy currents will not occur. The increase of the inductance phase error ϕ_s for high frequencies is more serious, but on the other hand it is possible to compensate it, not only for *one* but for *all* frequencies, by means of the condenser winding. It can readily be shown that while ϕ_m varies inversely as the frequency, the ratio of ϕ_s to ϕ_m varies directly as the square of the frequency, so that ϕ_s is directly proportional to the frequency like ϕ_s . Hence, it should prove possible by using a suitable condenser in conjunction with a special winding to neutralise the phase error of the instrument for all frequencies for which ϕ_m is negligible.

The Decomposition of Ozone by Heat.

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Much doubt has recently existed as to the interpretation which may be put upon measurements of the velocity of chemical change in gas reactions. Van't Hoff deduced the "order of the reaction" in certain cases from considerations of the law of mass action. Bone and Wheeler* have shown that the combination of hydrogen and oxygen at temperatures below that necessary to explode the mixture takes place mostly (if not entirely) at the surfaces with which the gases are in contact, and that no conclusion as to the order of the reaction can be drawn from pressure measurements.

Ozone was chosen for further work on the subject, as it affords one of the simplest possible cases. The decomposition by heat furnishes only one substance, and the reaction is irreversible (at least for all practical purposes).

Production of the Ozone.—The ozone was made by means of the usual Siemens' induction tube. Oxygen was obtained by heating potassium chlorate, and was stored over caustic potash solution. The ozonised oxygen was collected over sulphuric acid in a small gas-holder, consisting of two glass bulbs, each of about 350 c.c. capacity, and connected below by a U-tube. One of the bulbs was connected above with a three-way stop-cock, while the other bulb was open to the air through a calcium chloride tube.

The ozone was admitted from the induction tube to the gas-holder through one limb of the three-way stop-cock by means of a ground-glass joint. It was transferred by another ground-glass joint to the decomposition globe through the other limb of the stop-cock.

Apparatus for heating the Ozone.—The ozone was heated in a globe A, of about 350 c.c. capacity, by means of a bath of calcium chloride solution. The globe A was connected with the gauge C, and a similar globe B was connected with the gauge on the other side. The ozone was admitted through the ground-glass joint made at D, and the stop-cock E.

The large globe F and the pressure gauge G were used only for experiments under less than atmospheric pressure. H, K, L, and M represent two-way

* 'Phil. Trans.' A, vol. 206, p. 1.

diagonal stop-cocks, and N was a small ordinary stop-cock through which sulphuric acid was admitted to the gauge. The bath was heated by an Ostwald burner; it was thoroughly stirred, and the temperature maintained constant to $0^{\circ}.1$.

Method of conducting an Experiment.—The apparatus being in position (as in diagram) and the temperature steady, the globe A was exhausted by means of a Fleuss pump, the globe B being left open to the air. Ozonised oxygen was then transferred from the gas-holder to the globe A. Great care was taken to prevent any moist air from entering. The pressure was regulated so that A was filled at a pressure slightly greater than atmospheric. The excess was allowed to escape through D, the globe A was connected with the gauge, and readings of the pressure were taken at suitable intervals. In order to find the total amount of ozone present, the two globes and gauge were removed from the bath, and the globe A heated for 10 minutes with a Bunsen burner to about 300° (at the lowest part of the globe). In a trial experiment it was found that the ozone remaining after this treatment could be neglected. The apparatus was then replaced in the bath, and after the temperature had become steady, the pressure was read again.

Method of Calculation.—The pressure of the ozone at each reading was calculated as follows:—The actual pressure, as shown by the gauge, at each reading was subtracted from the final reading (when all the ozone was decomposed); double the number obtained gave the pressure of the ozone in millimetres of sulphuric acid.

A correction was then applied for the change of volume of the gases in A and B caused by the movement of the acid in the gauge. The correction was a small one, as the gauge tube was only 2 mm. in diameter.

The first or second order "constants" were then calculated in the usual way. Great difficulty was experienced in obtaining concordant results, especially with a new globe, which usually gave a greater rate of decomposition than did after some use.

The following results (p. 356, etc.) were obtained at various temperatures where t = time in minutes, x = amount of ozone decomposed (mm. H_2SO_4), a = initial pressure of ozone, K_1 is the first order constant

$\frac{1}{t} \log \frac{a}{a-x}$, and K_2 the constant of the second order $\frac{x}{t(a-x)a}$:—

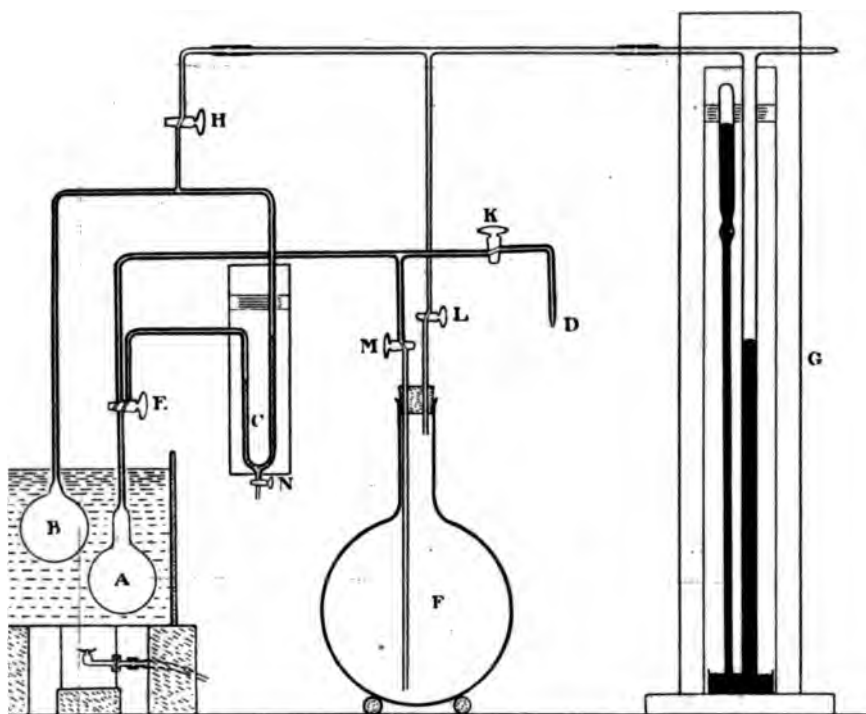


FIG. 1.

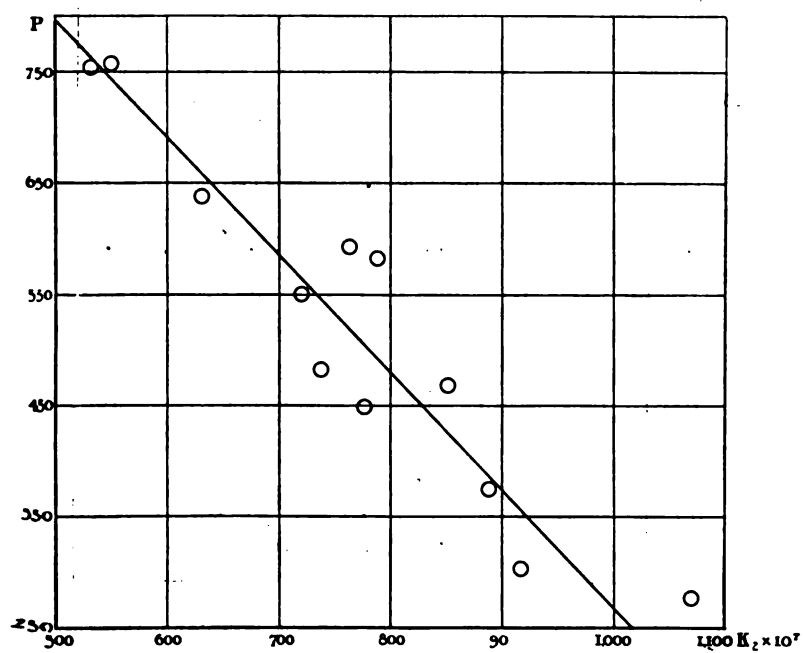


FIG. 2.

Temperature 119°.9. Globe II.

| t . | $a-x$. | x . | $K_2 \times 10^6$. | $K_1 \times 10^4$. |
|---------|---------|-------|---------------------|---------------------|
| 0 | 190.2 | | | |
| 2 | 152.7 | 37.5 | 646 | 477 |
| 3 | 137.4 | 52.8 | 673 | 471 |
| 4 | 124.3 | 65.9 | 697 | 462 |
| 6 | 105.4 | 84.8 | 705 | 427 |
| 8 | 89.2 | 101.0 | 744 | 411 |
| 13 | 64.5 | 125.7 | 788 | 361 |
| 18 | 49.5 | 140.7 | 830 | 325 |
| 28 | 33.3 | 156.9 | 885 | 270 |
| Mean... | | | 746 | |

Temperature 120°. Globe II.

| t . | $a-x$. | x . | $K_2 \times 10^6$. | $K_1 \times 10^4$. |
|---------|---------|-------|---------------------|---------------------|
| 0 | 227.2 | | | |
| 1 | 199.5 | 27.7 | 611 | 564 |
| 2 | 178.7 | 48.5 | 597 | 521 |
| 3 | 159.0 | 68.2 | 629 | 517 |
| 5 | 130.5 | 96.7 | 652 | 482 |
| 7 | 108.0 | 119.2 | 694 | 461 |
| 12 | 74.0 | 153.2 | 760 | 406 |
| 17 | 54.8 | 172.4 | 815 | 363 |
| 27 | 34.3 | 192.9 | 917 | 304 |
| Mean... | | | 709 | |

Temperature 100°. Globe II.

| t . | $a-x$. | x . | $K_2 \times 10^6$. | $K_1 \times 10^4$. |
|---------|---------|-------|---------------------|---------------------|
| 0 | 405.1 | | | |
| 2 | 388.8 | 16.3 | 518 | 90 |
| 4 | 372.5 | 32.6 | 540 | 91 |
| 6 | 358.2 | 46.9 | 539 | 89 |
| 11 | 326.2 | 78.9 | 543 | 85 |
| 16 | 299.3 | 105.8 | 545 | 82 |
| 26 | 255.4 | 149.7 | 557 | 77 |
| 41 | 210.2 | 194.9 | 558 | 69 |
| 61 | 168.1 | 237.0 | 570 | 63 |
| 96 | 121.9 | 283.2 | 597 | 54 |
| Mean... | | | 552 | |

Temperature 80°. Globe II.

| <i>t.</i> | <i>a - x.</i> | <i>x.</i> | $K_2 \times 10^3.$ | $K_1 \times 10^4.$ |
|-----------|---------------|-----------|--------------------|--------------------|
| 0 | 322.9 | | | |
| 15 | 311.4 | 11.5 | 762 | 105 |
| 30 | 301.1 | 21.8 | 748 | 101 |
| 45 | 289.9 | 33.0 | 738 | 104 |
| 60 | 280.2 | 42.7 | 736 | 103 |
| 90 | 262.9 | 60.0 | 735 | 99 |
| 120 | 247.0 | 75.9 | 733 | 97 |
| 180 | 220.3 | 102.6 | 801 | 92 |
| 240 | 198.7 | 124.2 | 806 | 88 |
| 300 | 180.0 | 142.9 | 819 | 85 |
| 360 | 164.5 | 158.4 | 829 | 81 |
| 420 | 151.1 | 171.8 | 838 | 79 |
| 508 | 135.4 | 187.5 | 844 | 74 |
| 568 | 125.2 | 197.7 | 857 | 72 |
| Mean... | | | 804 | |

Temperature 60°-15. Globe II.

| <i>t.</i> | <i>a - x.</i> | <i>x.</i> | $K_2 \times 10^3.$ | $K_1 \times 10^4.$ |
|-----------|---------------|-----------|--------------------|--------------------|
| 0 | 382.5 | | | |
| 180 | 361.2 | 21.3 | 856 | 139 |
| 330 | 344.2 | 38.3 | 881 | 139 |
| 1820 | 264.9 | 117.6 | 879 | 121 |
| 1533 | 251.9 | 130.6 | 884 | 118 |
| 1780 | 237.8 | 144.7 | 894 | 116 |
| 2046 | 224.8 | 157.7 | 897 | 113 |
| 2745 | 195.1 | 187.4 | 915 | 107 |
| Mean... | | | 887 | |

Temperature 40°. Globe II.

| <i>t.</i> | <i>a - x.</i> | <i>x.</i> | $K_2 \times 10^{10}.$ | $K_1 \times 10^7.$ |
|-----------|---------------|-----------|-----------------------|--------------------|
| 0 | 376.3 | | | |
| 675 | 368.4 | 7.9 | 844 | 136 |
| 1420 | 361.9 | 14.4 | 745 | 119 |
| 2055 | 356.2 | 20.1 | 730 | 116 |
| 2730 | 350.5 | 25.8 | 716 | 113 |
| 4170 | 338.6 | 37.7 | 710 | 110 |
| 5600 | 327.2 | 49.1 | 712 | 108 |
| 7040 | 317.4 | 58.9 | 700 | 105 |
| Mean... | | | 722 | |

correction has been applied for change of barometric pressure, or for the effect of pressure of the oxygen during the decomposition ; for, as will be seen the variations thus caused are within the limits of experimental error.

It will be noted that the results are not in close accordance with either a first or second order reaction; they are, however, considerably nearer the second than the first.* With one exception (at 40°) the value of $\frac{x}{t(a-x)}$ rises steadily throughout the experiment.

In the experiment at 40° the amount of ozone decomposed is very small and the measurements extend over several days, so that the decrease in "constant" may be due to experimental error.

The rate of decomposition increases roughly 10 times for a rise in temperature of 20° at the lower temperatures, and somewhat less rapidly at the higher temperatures.

Effect of varying the Extent of the Glass Surface.—Globe I was packed with short pieces of glass tube of a total area of about 1120 sq. cm. The internal area of the globe was about 240 cm., so that the area of the glass with which the ozone was in contact was nearly six times as large as before.

Temperature 119°9.

| <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^6.$ | <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^6.$ |
|-----------|-------------|-----------|--------------------|-----------|-------------|-----------|--------------------|
| 0 | 272.5 | | | 4 | 176.2 | 96.3 | 501 |
| 1 | 240.3 | 32.2 | 492 | 6 | 149.4 | 123.1 | 504 |
| 2 | 213.5 | 59.0 | 507 | 11 | 109.3 | 163.2 | 498 |
| 3 | 193.7 | 78.8 | 498 | | | Mean.... | 500 |

The corresponding mean value for the globe with the tubes is 117×10^{-6} ; thus the rate of decomposition was 4.27 as fast. Both the bulb and the tubes were made of soft soda glass. It will be noted that the rate appears much more constant owing to the increased glass surface, but this may be due simply to the increased rate and consequent shortening of the time intervals.

A similar experiment at about 80° gave the following result:—

Temperature 79°9. Globe II.

| <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^6.$ | <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^6.$ |
|-----------|-------------|-----------|--------------------|-----------|-------------|-----------|--------------------|
| 0 | 308.0 | | | 6 | 186.0 | 142.0 | 463 |
| 1 | 268.8 | 39.2 | 473 | 8 | 144.3 | 163.7 | 460 |
| 2 | 238.2 | 69.8 | 476 | 13 | 107.5 | 200.5 | 466 |
| 3 | 215.2 | 92.8 | 467 | 23 | 68.1 | 239.9 | 497 |
| 4 | 196.2 | 111.8 | 462 | | | | |

* Cf. Warburg, 'Sitzungsberichte der Königl. Preuss. Akad. Wiss. Berlin,' 1901, vol. 48, p. 1126.

the mean rate with the same globe at 80° is 8.04×10^{-6} , so that at this temperature the rate was increased nearly 60 times by the glass tubes.

In another experiment the globe was loosely packed with glass wool, with following result:—

Temperature 40° . Globe III.

| <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^7.$ | <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^7.$ |
|-----------|-------------|-----------|--------------------|-----------|-------------|-----------|--------------------|
| 0 | 283.4 | | | 55 | 213.1 | 70.8 | 212 |
| 5 | 275.1 | 8.3 | 213 | 70 | 199.4 | 84.0 | 212 |
| 10 | 266.8 | 16.6 | 220 | 90 | 181.1 | 102.3 | 221 |
| 20 | 252.2 | 31.2 | 218 | 120 | 158.8 | 124.6 | 231 |
| 30 | 239.2 | 44.2 | 217 | 150 | 140.7 | 142.7 | 239 |
| 40 | 228.6 | 54.8 | 211 | 210 | 109.8 | 173.6 | 266 |
| Mean... | | | | | | | 224 |

the normal rate for the globe was not determined at this temperature, but at 00° it was 0.00013. Calculating from the ratio of the rates observed with be II, this gives a rate 1.74×10^{-7} at 40° , so that the presence of the wool increased the rate of decomposition 129 times.

The effect of a porous substance was next tried, the globe being filled with pieces of clay-pipe stem. The rate of decomposition was then so rapid (not owing to the very large surface) that it was found impossible to measure it, even at the ordinary temperature.

In order to obtain a rate that would be measurable, six pieces of pipe of about 2 inches in length were placed at the bottom of the globe. The following numbers were then obtained:—

Temperature $99^{\circ}.7$.

| <i>t.</i> | <i>a-x.</i> | $K_1 \times 10^4.$ | <i>t.</i> | <i>a-x.</i> | $K_1 \times 10^4.$ |
|-----------|-------------|--------------------|-----------|-------------|--------------------|
| 0 | 188.2 | | 5 | 85.6 | 684 |
| 1.25 | 155.6 | 661 | 7 | 63.3 | 676 |
| 2 | 138.1 | 672 | 9 | 46.6 | 674 |
| 3 | 117.8 | 678 | 14 | 22.0 | 666 |
| 4 | 100.0 | 687 | 24 | 5.1 | 653 |

Temperature $60^{\circ}.1$.

| <i>t.</i> | <i>a-x.</i> | $K_1 \times 10^4.$ | <i>t.</i> | <i>a-x.</i> | $K_1 \times 10^4.$ |
|-----------|-------------|--------------------|-----------|-------------|--------------------|
| 0 | 302.7 | | 7 | 150.1 | 435 |
| 1 | 273.8 | 435 | 9 | 123.0 | 435 |
| 2 | 247.0 | 442 | 15 | 70.6 | 421 |
| 3 | 222.0 | 449 | 26 | 27.3 | 402 |
| 4 | 200.4 | 448 | 36 | 11.2 | 398 |
| 5 | 181.3 | 445 | | | |

These numbers extend over a wide range and clearly indicate a reaction "of the first order."

The effect of certain metallic oxides was then tried; a few grammes of the oxide were placed at the bottom of the globe. For each change of material, the globe was cut at the neck and resealed after the introduction of the substance.

Temperature 99°·7. About 20 grammes granulated CuO in Globe.

| t . | $a-x$. | x . | $K_2 \times 10^4$. | $K_1 \times 10^4$. |
|-------|---------|-------|---------------------|---------------------|
| 0 | 257·8 | | | |
| 1 | 208·8 | 49·0 | 91 | 917 |
| 2 | 178·5 | 88·8 | 94 | 856 |
| 3 | 147·6 | 109·7 | 96 | 804 |
| 4 | 126·6 | 130·7 | 100 | 770 |
| 5 | 109·4 | 147·9 | 106 | 743 |
| 6 | 96·0 | 163·8 | 110 | 721 |
| 7 | 83·2 | 174·1 | 116 | 700 |
| 9 | 68·8 | 194·0 | 122 | 677 |
| 11 | 47·4 | 209·9 | 156 | 668 |
| 16 | 28·2 | 234·1 | 245 | 653 |
| 21 | 10·7 | 246·6 | 427 | 657 |

The numbers show that the reaction is in this case much nearer first order than second, but is not in close agreement with either. In another experiment at a lower temperature, a good first order constant was obtained:—

Temperature 40°·5. About 20 grammes granulated CuO in Globe.

| t . | $a-x$. | $K_1 \times 10^4$. | t . | $a-x$. | $K_1 \times 10^4$. |
|-------|---------|---------------------|-------|---------|---------------------|
| 0 | 342·6 | | 7 | 196·0 | 346 |
| 1 | 314·8 | 368 | 8 | 181·3 | 345 |
| 2 | 289·9 | 362 | 10 | 155·2 | 344 |
| 3 | 266·6 | 363 | 12 | 134·7 | 338 |
| 4 | 247·5 | 353 | 17 | 93·3 | 332 |
| 5 | 227·6 | 355 | 28 | 38·6 | 339 |
| 6 | 211·0 | 351 | 38 | 15·2 | 356 |

A similar result was obtained with magnesia, but the rate was so fast that it was very difficult to measure.

Temperature 40°. About 10 grammes MgO.

| t . | $a-x$. | $K_1 \times 10^3$. | t . | $a-x$. | $K_1 \times 10^3$. |
|-------|---------|---------------------|-------|---------|---------------------|
| 0 | 34·1 | | 3 | 7·7 | 215 |
| 1 | 20·9 | 213 | 4 | 5·0 | 208 |
| 2 | 12·4 | 220 | 7 | 1·9 | 179 |

Manganese peroxide also decomposes ozone at an extremely rapid rate, as shown by the following results :—

Temperature 40°. 10 grammes MnO_2 , in small lumps, in Globe.

| $t.$ | $a-x.$ | $K_1 \times 10^3.$ | $t.$ | $a-x.$ | $K_1 \times 10^3.$ |
|------|--------|--------------------|------|--------|--------------------|
| 0.0 | 151.8 | | 2.0 | 27.8 | 867 |
| 0.5 | 102.0 | 345 | 2.5 | 17.6 | 872 |
| 1.0 | 67.0 | 354 | 3.5 | 6.6 | 886 |
| 1.5 | 42.7 | 367 | | | |

Temperature 15°. 10 grammes MnO_2 .

| $t.$ | $a-x.$ | $K_1 \times 10^3.$ | $t.$ | $a-x.$ | $K_1 \times 10^3.$ |
|------|--------|--------------------|------|--------|--------------------|
| 0.0 | 149.7 | | 3.5 | 32.2 | 190 |
| 0.5 | 119.4 | 195 | 4.5 | 21.0 | 189 |
| 1.0 | 94.8 | 198 | 5.5 | 13.6 | 189 |
| 1.5 | 75.7 | 197 | 7.5 | 6.3 | 183 |
| 2.5 | 49.2 | 198 | 9.5 | 2.1 | 195 |

Lead peroxide, on the other hand, was found to have comparatively little effect on the rate of decomposition. Commercial lead peroxide was found to absorb ozone, no doubt owing to the presence of lower oxides. The following numbers were obtained with specially purified peroxide, which had been allowed to stand in the presence of ozone :—

Temperature 60°. 1 gramme PbO_2 , in Powder.

| $t.$ | $a-x.$ | $x.$ | $K_2 \times 10^6.$ | $K_1 \times 10^4.$ |
|------|--------|-------|--------------------|--------------------|
| 0 | 421.4 | | | |
| 17 | 396.7 | 24.7 | 869 | 154 |
| 37 | 371.2 | 50.2 | 867 | 149 |
| 57 | 347.4 | 74.0 | 887 | 147 |
| 87 | 316.0 | 105.4 | 910 | 144 |
| 167 | 248.6 | 172.8 | 987 | 137 |
| 207 | 221.7 | 199.7 | 1033 | 135 |

The normal rate at 60°, calculated in the same way as for 40°, is 209×10^{-8} .

Effect of Metallic Surfaces.—Consistent results were not obtained unless the metal had been previously heated in the presence of ozone.

The normal rate for the globe is 1220×10^{-7} , so that the presence of the platinum appears actually to diminish the rate. It is probable that the

normal rate for the globe had changed owing to the alteration in the neck during the opening and resealing.

Temperature 99°·7. Total Area of Surface of Platinum Foil, 19·5 sq. cm.

| <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^7.$ | <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^7.$ |
|-----------|-------------|-----------|--------------------|-----------|-------------|-----------|--------------------|
| 0 | 435·0 | | | 9 | 360·0 | 75·0 | 532 |
| 1 | 425·6 | 9·4 | 508 | 14 | 328·8 | 106·2 | 530 |
| 2 | 417·2 | 17·8 | 490 | 19 | 300·5 | 134·5 | 541 |
| 3 | 407·9 | 27·1 | 509 | 24 | 275·7 | 159·3 | 554 |
| 5 | 391·2 | 43·8 | 515 | 34 | 236·6 | 198·4 | 567 |
| 7 | 375·7 | 59·3 | 518 | 56 | 178·8 | 256·2 | 588 |

Similar results were obtained in the case of nickel:—

Temperature 99°·8. Total Area of Surface of Nickel Foil, 71·5 sq. cm.

| <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^7.$ | $K_1 \times 10^4.$ |
|-----------|-------------|-----------|--------------------|--------------------|
| 0 | 365·8 | | | |
| 2 | 350·7 | 15·1 | 588 | 92 |
| 4 | 336·0 | 29·8 | 606 | 93 |
| 10 | 295·0 | 70·8 | 656 | 93 |
| 18 | 254·0 | 111·8 | 668 | 88 |
| 30 | 207·4 | 158·4 | 696 | 82 |
| 52 | 155·6 | 210·2 | 710 | 71 |
| 72 | 124·6 | 241·2 | 735 | 65 |
| 112 | 86·0 | 279·8 | 794 | 56 |

Some experiments were carried out with silver foil, but the rate of decomposition could not be measured owing to the gradual oxidation of the silver to peroxide by the action of the ozone.

An experiment with platinum black showed an acceleration of the rate of decomposition, though not a large one, and a "second order" constant was obtained.

Temperature 99°·7. Globe VI. About 2 grammes Platinum Black.

| <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^6.$ | <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^6.$ |
|-----------|-------------|-----------|--------------------|-----------|-------------|-----------|--------------------|
| 0 | 98·8 | | | 23 | 59·0 | 39·8 | 297 |
| 3 | 89·8 | 9·0 | 388 | 33 | 50·6 | 48·2 | 292 |
| 8 | 79·2 | 19·6 | 313 | 53 | 38·0 | 60·8 | 305 |
| 13 | 70·6 | 28·2 | 311 | 88 | 26·5 | 72·3 | 314 |

The normal rate for this globe was $81·9 \times 10^{-6}$.

Influence of Moisture.—A trace of moisture is known to be held by a glass surface, even at temperatures above 100°. An experiment was therefore

made to discover whether the moisture so held was sufficient to have an appreciable effect on the rate of decomposition. The globe was heated in an air bath at about 400°, and pumped out several times. It was then placed in the calcium chloride bath, and an experiment conducted as usual. The mean rate was 0·000055, while the rate found without the previous heating was 0·000053, a difference which may be ascribed to experimental error.

A series of experiments was made with varying quantities of moisture in the globe. The water vapour was introduced from a nitrometer containing water. This was well shaken to ensure the saturation of the air with water vapour; it was then connected with the exhausted globe, and the required quantity of moist air quickly admitted, the pressure of the air being maintained constant.

In one experiment air was passed from the nitrometer through a series of four bulbs containing water, placed in a water bath, and thence into the decomposition globe. In this way, 2·77 milligrammes of water vapour were introduced.

The general effect of the moisture is to quicken the rate of decomposition, and the numbers are in much better accord with a second order constant than those obtained with dry ozone. The following is a good example:—

Temperature 119°·5. Globe I. 0·69 milligramme Water in Globe.

| <i>t.</i> | <i>a</i> - <i>x.</i> | <i>x.</i> | $K_2 \times 10^4.$ | <i>t.</i> | <i>a</i> - <i>x.</i> | <i>x.</i> | $K_2 \times 10^4.$ |
|-----------|----------------------|-----------|--------------------|-----------|----------------------|-----------|--------------------|
| 0 | 329·0 | | | 8 | 225·3 | 103·7 | 175 |
| 1 | 311·3 | 17·7 | 173 | 13 | 188·7 | 140·3 | 174 |
| 2 | 294·0 | 35·0 | 181 | 23 | 142·9 | 186·1 | 172 |
| 3 | 279·9 | 49·1 | 178 | 33 | 114·0 | 215·0 | 174 |
| 4 | 266·1 | 62·9 | 180 | 53 | 80·8 | 248·2 | 176 |
| 6 | 244·2 | 84·8 | 176 | | | Mean..... | 176 |

The increase in the rate of decomposition is (within the limits of experimental error) proportional to the mass of water vapour present. The mean values of the constants are here given, together with the corresponding quantities of water admitted in milligrammes (*m*), and the constants calculated from the formula:

$$k = 122 + 135 \cdot 1m.$$

The normal rate for the globe was 0·000122.

| <i>m.</i> | $K_2 \times 10^4.$ | <i>k.</i> | <i>m.</i> | $K_2 \times 10^4.$ | <i>k.</i> |
|-----------|--------------------|-----------|-----------|--------------------|-----------|
| 0·0 | 122 | | 0·58 | 209 | 200 |
| 0·75 | 214 | 223 | 1·40 | 310 | 324 |
| 0·69 | 176 | 215 | 2·77 | 515 | 496 |

Effect of Nitric Oxide.—An attempt was made to measure the rate of decomposition of ozone after the addition of a small quantity of nitric oxide. Several trials were necessary in order to find a suitable temperature, and how much nitric oxide could be added without decomposing the ozone too quickly. Finally, measurements were made at $119^{\circ}1$ after the addition of 0.2 c.c. nitric oxide (at 15° and 800 mm.). The nitric oxide was made in a nitrometer from potassium nitrate and sulphuric acid over mercury, and was forced into the globe, which already contained ozonised oxygen at a constant temperature.

The following is the result:—

| <i>t.</i> | <i>a-x.</i> | <i>x.</i> | $K_2 \times 10^3.$ | $K_1 \times 10^3.$ |
|-----------|-------------|-----------|--------------------|--------------------|
| 0 | 58.5 | | | |
| 1 | 43.4 | 15.1 | 595 | 130 |
| 2 | 30.5 | 28.0 | 785 | 141 |
| 3 | 21.5 | 37.0 | 961 | 145 |
| 4 | 13.7 | 44.8 | 1397 | 158 |

The rate of decomposition was thus extremely fast, and, so far as it could be followed, appeared to be roughly of the first order.

In a similar experiment with 1 c.c. of nitric oxide, the decomposition was too rapid for measurements to be made.

Attempts were made to follow the change completely at a lower temperature; 0.8 c.c. nitric oxide, contained in a tube between two stop-cocks, was allowed to diffuse into a bulb containing 150 c.c. ozonised oxygen, the whole being placed in a water bath at 10° .

The change of pressure was measured by a sulphuric acid gauge connected with the upper part of the bulb. It was found that a decrease of pressure of 47 mm. of sulphuric acid took place, the pressure then remaining constant. This represents a decrease of about 1 per cent. in the volume, and is more than would be accounted for by the combination of nitric oxide either with oxygen or ozone to form nitrogen peroxide. Probably this is due to condensation of nitrogen tetroxide in the liquid state.

At 50° no rapid decomposition of the ozone was observed after introducing 1 c.c. of nitric oxide, while at 100° the rate was accelerated but very irregularly.

Effect of Varying the Pressure of the Oxygen.—A series of experiments was made at various pressures with the complete apparatus as shown in fig. 1. The large globe F was connected with B, and brought down to the required pressure by means of a Fleuss pump. A was exhausted and the ozone admitted in the usual way, until the pressure in A was known to be

in excess of that required. The globe A was connected with F until the pressure was equalised; it was then connected with the gauge, the stop-cock H was closed, and readings were taken as usual. The total amount of ozone was also determined as before.

Some manganese peroxide was placed at the bottom of the globe F in order to decompose the ozone admitted.

The general character of the results is the same as those at atmospheric pressure, *i.e.*, they are approximately of the second order, but the rate increases towards the end of the experiment. The mean results are given in the following table, together with two at ordinary pressure for comparison:—

Temperature 99°·7.

| Pressure. | $K_2 \times 10^7$. | Pressure. | $K_2 \times 10^7$. | Pressure. | $K_2 \times 10^7$. |
|-----------|---------------------|-----------|---------------------|-----------|---------------------|
| 755 | 531 | 583 | 788 | 449 | 776 |
| 758 | 550 | 550 | 720 | 375 | 888 |
| 638 | 631 | 482 | 737 | 304 | 916 |
| 593 | 763 | 468 | 851 | 276 | 1070 |

Effect of Diluting with Air.—A few experiments were made in which the pressure of the oxygen was diminished by the addition of air. The large globe F was exhausted to approximately $\frac{1}{2}$ an atmosphere; the globe A was then filled as usual and allowed to blow off into F. The following are the results:—

Temperature 99°·8.

| Pressure of oxygen. | $K_2 \times 10^6$. |
|---------------------|---------------------|
| mm. | |
| 467 | 155 |
| 458 | 165 |
| 462 | 152 |

Normal rate for the globe (VI), 81.9×10^{-6} .

Discussion of Results.

Effect of Temperature.—The relation between rate of decomposition and temperature may be expressed by the formula $\log k = a + bt$, a formula found by one of us to express the connection between the rate of evaporation of ammonia from aqueous solution and temperature* and used also by Van't Hoff.†

* 'Chem. Soc. Trans,' 1898, p. 524.

† 'Vorlesungen über theoretische und physikalische Chemie,' 1901, vol. 1, p. 224.

Putting $a = 2.86$ and $b = 0.05$, the following numbers are obtained:—

| Temperature. | $\log k$ (found). | $\log k$ (calculated). |
|--------------|-------------------|------------------------|
| 40 | 2.86 | 2.86 |
| 60 | 3.95 | 3.86 |
| 80 | 4.91 | 4.86 |
| 100 | 5.74 | 5.86 |
| 120 | 6.86 | 6.86 |

It occurred to us that the decomposition might take place instantaneously at the surface of the glass (or other substance), and that the rate measured was simply the rate of diffusion of the gas towards the surface. These results, however, show that the idea is untenable, for the rate would in that case vary as the square root of the absolute temperature.

Effect of Varying Extent of Surface.—It has been shown that the rate depends on the extent of the surface, but it could not be shown that it is proportional to the surface. It must be remembered, however, that it is impossible to vary the extent of the surface and yet ensure its uniformity. With a very large surface a much better second order constant is obtained; this may be due to the almost entire prevention of any effect of diffusion, but we are inclined to think that it is caused simply by the increased rapidity and shorter range of the reaction.

Effect of Oxides.—From the results given it is impossible to conclude that the peroxides used act as carriers of oxygen, for lead peroxide has but little effect, whereas manganese peroxide accelerates the reaction enormously. Moreover, copper oxide and magnesium oxide have a great effect in increasing the rate of decomposition. Neither can the effect be due entirely to the extent of the surface of the oxide. Manganese peroxide in lumps had more effect than magnesia in powder, but lead peroxide in powder had very little influence. With these oxides a good first order constant was obtained, i.e., the rate of decomposition was proportional to the pressure of the ozone, and it seems to us that the only conclusion to be drawn is that the real factor is the rate of absorption or condensation of ozone on the surface of the oxide.

Effect of Metallic Surfaces.—Of the metals tried, the effect in each case was small, and appeared to be a diminution of the rate of decomposition. This is entirely different from the effect of metals on the combination of hydrogen and oxygen as found by Bone and Wheeler;* the latter was attributed, however, to the occlusion of hydrogen.

Effect of Certain Vapours.—It has been shown that water vapour

* *Loc. cit.*

accelerates the rate of decomposition, and that the effect is roughly proportional to the quantity of water present. Ozone is not known to have any action on water vapour, and it appears probable that this effect is due to the deposition of moisture on the surface of the glass, owing to which the ozone would be more rapidly condensed. These results appear to be directly in opposition to those of Shenstone, who found that ozone was more stable in the presence of moisture (this was, however, at a much lower temperature).

The action of nitric oxide is much greater than that of water if a sufficiently high temperature is employed (100° — 120°), and it would seem a reasonable explanation that the nitric oxide acts as a carrier of oxygen, being continually oxidised to the peroxide, and reduced again by the action of the ozone until the latter is entirely decomposed.

Effect of Variation of the Oxygen Pressure.—The rate of decomposition has been shown to be a linear function of the pressure of the oxygen; this cannot be caused by the reversibility of the reaction, for it has been shown to be irreversible for all practical purposes. S. Jahn* made somewhat similar experiments, varying the pressure of the oxygen by dilution with air, and found that the rate varies approximately inversely as the oxygen pressure, a result confirmed by experiments of our own. From these results Jahn deduces that a secondary reaction takes place, $O_3 + O = 2O_2$. We find that on varying the pressure without the intervention of another gas, the rate is not affected to the same extent, *e.g.*, a variation of the pressure from 600 mm. to 300 mm. caused the rate to vary from 0.0000685 to 0.000097. We are inclined to think that Jahn's conclusion is not justifiable, and that the variation of the oxygen pressure produces a difference in the gas-film on the surface and so alters the rate. It can only be said at present that the mechanism of the process is not understood.

Reversibility of the Reaction.—Attempts were made to synthesise ozone by passing a slow stream of oxygen through a combustion tube heated in a gas furnace. The tube was bent at the outlet and dipped in a solution of potassium iodide and starch. No ozone could be detected. The experiment was then repeated with the following substances in the tube respectively:—pipe stems, iron nails, platinised asbestos, manganese peroxide: traces of ozone were formed with the last named, but none could be detected with the others. The solution became brown, and on letting it stand a blue colour was developed. No ozone was found unless the temperature was high (a low red heat), and the oxygen was passed through quickly. With a slow stream probably the ozone formed was decomposed before leaving the tube.

* 'Zeit. anorg. Chem.,' 1906, vol. 48, p. 260.

In the following experiments oxygen was heated in a globe for many hours in order to discover whether any ozone could be formed in this way :—

| Temperature. | Time of heating, etc. | Result. |
|--------------|------------------------------|-----------------------------|
| ° | | |
| 130 | 24 hours | Nil |
| 100 | 17 " | " |
| 100 | 4 days with Pt black | " |
| 100 | 4 days with MnO ₂ | " |
| 100 | 7 days | Trace of O ₃ (?) |
| 100 | 14 " | " " |

It is somewhat doubtful whether any ozone was detected, for a blank experiment with oxygen (not heated) gave nearly as much colour, *i.e.*, a brownish tint, developing into blue on standing some hours.

* Experiments were also made to ascertain whether ozone could be completely decomposed by heat ; the following are the results :—

| Temperature. | Time of heating. | Result. |
|--------------|------------------|---|
| ° | | |
| 100 | 18 hours | 1·7 milligrammes O ₃ remained. |
| 100 | 5 days | 0·07 " " |
| 100 | 14 " | Trace " " |

In the last experiment there was no doubt that a trace of ozone remained after a fortnight's heating ; it seems probable that it had come into equilibrium. We conclude from these experiments that the decomposition of ozone by heat is not completely irreversible at 100°, but that the reverse reaction is so small that it is difficult to detect.

Summary.—The rate of decomposition of ozone has been measured under various conditions with the following results :—

1. In a glass vessel the reaction is approximately of the second order.
2. The relation between the rate of decomposition and temperature may be expressed by the formula $\log k = a + bt$.
3. The rate of decomposition is very largely influenced by the extent of the surface with which the ozone is in contact.
4. The reaction is of the first order when the ozone is in contact with a porous substance (clay-pipe stems) or some oxides.
5. Metallic surfaces have but little effect on the decomposition.
6. Water vapour accelerates the decomposition, and the acceleration is proportional to the amount present.

7. Nitric oxide greatly accelerates the decomposition.
8. The rate of decomposition is a linear function of the oxygen pressure. A greater effect is produced by diluting with nitrogen than by simply reducing the pressure of the oxygen.
9. At 100° the reaction appears to be very slightly reversible.
10. Finally, the decomposition appears to take place mainly (if not entirely) at the surfaces with which the ozone is in contact, and pressure measurements give no indication of the number of molecules reacting.

The expense incurred in this investigation has been defrayed by a grant from the Royal Society.

*Effects of Self-induction in an Iron Cylinder when traversed
by Alternating Currents.**

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(Communicated by Sir William Preece, F.R.S. Received January 23,—Read
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In a previous paper† the effects of self-induction in an iron cylinder were studied when a continuous current flowing through the cylinder in a direction parallel with its axis of figure was suddenly reversed and again maintained steady. In the experiments reported in the present paper the currents in the cylinder were made to alternate in the following manner. A continuous current dynamo, capable of giving currents up to 2000 amperes or more, was weakly excited and its brushes were short-circuited by the cylinder to be experimented upon in series with the shunt of a moving-coil ampere-meter. The brushes were moved round the commutator by aid of a worm and worm-wheel from the position of maximum to that of zero current. The field was then reversed and the brushes moved back to their initial position.

By continuing these operations an alternating current was caused to flow through the cylinder, and its periodic time was controlled by the speed at which the brushes were moved. The worm axle was uniformly rotated by hand at a speed determined by the operator listening to a seconds clock.

* In connection with this research, I wish to acknowledge a grant voted to me by the Council of the Royal Society out of the Government Grant Fund.

† 'Roy. Soc. Proc.,' A, vol. 78, p. 22, 1906.

Simultaneously readings were taken at known epochs on (a) each of three dead-beat galvanometers connected to exploring coils threaded through holes in the mass of the cylinder for the purpose of obtaining the E.M.F.'s at different depths due to the rate of change of the magnetic induction, and on (b) the moving-coil ampere-meter.

The cylinder is of mild steel and has a diameter and length each equal to 10 inches (25.4 cm.). It is provided with holes drilled in a plane containing its axis of figure in such manner that exploring coils could be threaded to enclose certain portions of that plane. The coils are referred to respectively as 1, 2, 3, and are each 2 inches wide in a direction parallel with the axis of figure and mid-way between the ends of the cylinder. Their depths in a radial direction are respectively 1, 2, and 2 inches and therefore their average radii are 0.5, 2, and 4 inches respectively. The current was passed into the cylinder by aid of the massive gunmetal castings used in the experiments previously described.* The deflections of the galvanometers have been reduced to volts per turn per square centimetre and are plotted in the case of two of the experiments in figs. 1 and 2. The curves are numbered 1, 2, 3 to correspond with the particular coils from which they were obtained. Time progresses from left to right of each figure.

Magnetic Induction (B) as affected by Variation of Periodic Time and Total Current.—On integrating the E.M.F. curves the magnetic induction (B) has been obtained. In Table I, where the results are summarised, the maximum average values of the magnetic induction are set forth. Looking at the values of the maximum induction for periodic time 0.75 minute, and maximum total currents of 1000 and 2000 amperes, we notice how great is the shielding effect in the former case as compared with the latter. This effect is intimately connected with the average permeability of the iron, which, as will be shown, is higher with a maximum total current of 1000 amperes. A comparison of the maximum values of the magnetic induction for periodic time 0.75 minute and maximum total current of 500 and 1000 amperes shows that in those two cases the innermost coil is equally affected. For a maximum total current of 1000 amperes the percentage diminution of maximum B for coil 1 as the periodic time is varied from 6 to 0.75 minute is much greater than in the case of maximum total currents of 500 and 2000 amperes. It should be noted that in Table I the total amperes are given approximately, their accurate values are given in Table II.

Wave-form and Phase Displacement as affected by Variation of Periodic Time and Total Current.—Figs. 1 and 2 are given as showing two extreme cases. In each diagram c_1 , c_2 , c_3 are the currents interior to the radii $\frac{1}{2}$, 2, and 4 inches

* See 'Roy. Soc. Proc.' vol. 69, p. 440, fig. 1.

spectively. In fig. 1 the periodic time is 6 minutes and the total current 1000 amperes, and the shielding effect is comparatively small. In fig. 2 the periodic time is 0.75 minute and the total current 1000 amperes, and this

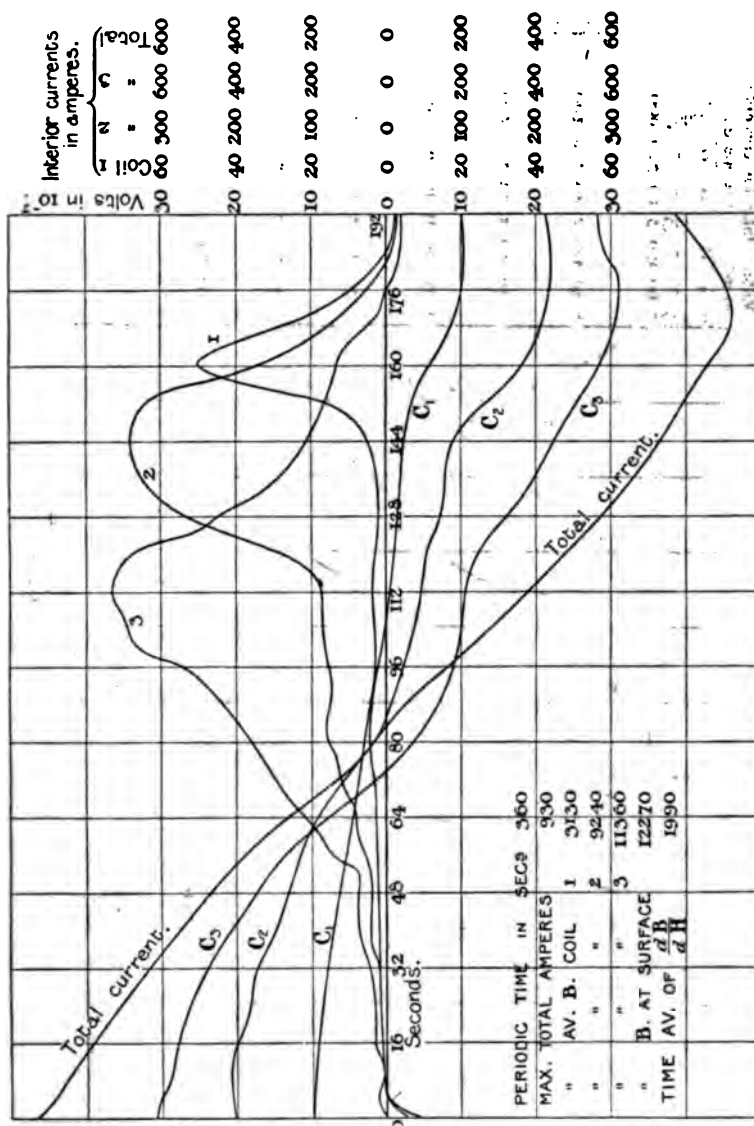


FIG. 1.

one case in which the centre of the cylinder is practically devoid of current. may be generally remarked that, referring the phase displacement of the M.F. curves to the maximum of current for a given frequency, the maximum M.F. occurs earlier as the current is increased. For a given total current

the maximum of E.M.F. occurs later as the frequency is increased. The wave-forms of the E.M.F.'s are very much more peaked for the higher currents and the longer periodic times. The peaks of the E.M.F. curves cease to be so prominent at the high frequencies, but they are retained more with the large total currents than with the small ones.

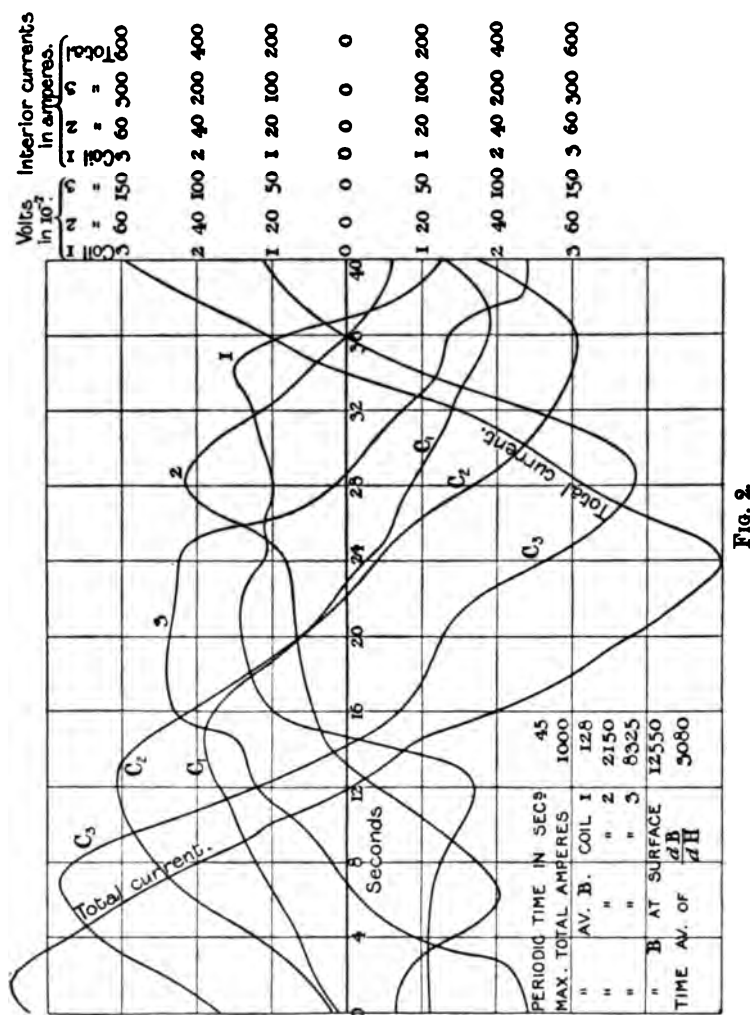


Fig. 2

Energy dissipated by Electric Current in overcoming Resistance and by Magnetic Hysteresis.—For the varying conditions of frequency and total current the C^2R watts per centimetre length of the cylinder have been calculated and compared with the C^2R watts which would be found, if a continuous current equal in value to the root-mean-square value of the

Table I.—Maximum Average Induction B and Average Permeability.

| Maximum total amperes.* | Periodic time in minutes. Frequency | 0.75. | 1.5. | 3. | 6. |
|-------------------------|--|--------|--------|--------|--------|
| | | 1/45. | 1/90. | 1/180. | 1/360. |
| 2000 | { Coil 1 | 3,460 | 4,440 | 4,730 | 8,960 |
| | B { Coil 2 | 6,050 | 12,000 | 12,640 | 12,040 |
| | Coil 3 | 12,600 | 14,080 | 14,160 | 13,560 |
| | B at surface of cylinder | 14,240 | 14,380 | 14,380 | 14,340 |
| | Permeability | 2,520 | 2,800 | 2,140 | 1,260 |
| 1500 | { Coil 1 | 208 | | | |
| | B { Coil 2 | 4,460 | | | |
| | Coil 3 | 8,940 | | | |
| | B at surface of cylinder | 13,780 | | | |
| | Permeability | 3,050 | | | |
| 1000 | { Coil 1 | 128 | 680 | 2,040 | 3,130 |
| | B { Coil 2 | 2,150 | 6,200 | 8,200 | 9,240 |
| | Coil 3 | 8,325 | 10,620 | 11,100 | 11,360 |
| | B at surface of cylinder | 12,550 | 12,480 | 12,150 | 12,270 |
| | Permeability | 3,080 | 3,060 | 2,690 | 1,990 |
| 500 | { Coil 1 | 128 | 215 | 294 | 576 |
| | B { Coil 2 | 880 | 2,070 | 3,240 | 4,736 |
| | Coil 3 | 4,580 | 5,500 | 6,620 | 6,940 |
| | B at surface of cylinder | 8,400 | 7,300 | 7,250 | 7,000 |
| | Permeability | 2,010 | 2,260 | 2,310 | 2,130 |

* These are approximate values. For accurate values, see Table II.

† Fig. 2.

‡ Fig. 1.

alternating current were allowed to traverse the cylinder: (a) on the assumption of constant current density; (b) having regard to the variation of current density which was found actually to exist, owing to end effect. An attempt is made to compare the ratios obtained with the average permeability of the material under the conditions of test. The watts due to magnetic hysteresis have also been calculated, and a comparison made between them and the watts which would be found if the distribution of magnetic induction under continuous current were assumed to persist at the particular frequency. By a different application of the same principles, an attempt has been made to check the values of the total watts due to C^2R and magnetic hysteresis found separately. Finally, the ratios of the watts due to C^2R and to magnetic hysteresis are given. The results are set forth in Table II.

(1) The C^2R watts have been calculated as follows. The E.M.F. curves previously integrated have been used to give the average value of the magnetic induction (B) over the three annuli at any instant of time. From the hysteresis loops for the material, obtained by the ballistic galvanometer, the corresponding values of H have been obtained. In finding the currents from

Table II.

| Frequency. | Total current in amperes. | | C ² R loss per cm. length of cylinder in watts. | | | | | Average permeability. | Watts lost by magnetic hysteresis per cm. length, in 10 ⁻³ . | Total watts per cm. length, in 10 ⁻³ . | Ratio C ² R/hysteresis = A/D. |
|--------------------|------------------------------|---------------|---|---|------------|--|------------|-----------------------|---|---|--|
| | Max. value. | R.M.S. value. | Alternate current, in 10 ⁻³ . | Continuous current, uniform distribution, in 10 ⁻³ . | Ratio A/B. | Continuous current, actual distribution, in 10 ⁻³ . | Ratio A/C. | | | | |
| 1/45 (0.0222) | 1860 | 1200 | A. 4700 | B. 3390 | 1.39 | C. 3790 | 1.24 | 2520 | D. 824 | 5520 | 5.74 |
| | 1520 | 915 | 2970 | 1985 | 1.50 | 2220 | 1.34 | 3050 | 663 | 3630 | 4.48 |
| | 1000* | 598 | 1490 | 847 | 1.76 | 947 | 1.57 | 3080 | 381 | 1870 | 3.90 |
| | 500 | 299 | 325 | 212 | 1.53 | 237 | 1.37 | 2010 | 169 | 494 | 1.92 |
| 1/90 (0.0111) | 2000 | 1270 | 4770 | 3830 | 1.25 | 4280 | 1.12 | 2800 | 540 | 5310 | 8.85 |
| | 980 | 627 | 1230 | 930 | 1.32 | 1040 | 1.18 | 3060 | 298 | 1530 | 4.12 |
| | 430 | 269 | 238 | 171 | 1.39 | 191 | 1.24 | 2260 | 97 | 335 | 2.46 |
| 1/180 (0.00556) | 2000 | 1260 | 4680 | 3730 | 1.25 | 4160 | 1.12 | 2140 | 286 | 4960 | 16.4 |
| | 900 | 588 | 1030 | 819 | 1.25 | 915 | 1.12 | 2690 | 175 | 1200 | 5.88 |
| | 435 | 267 | 226 | 169 | 1.34 | 189 | 1.20 | 2310 | 69 | 295 | 3.28 |
| 1/360 (0.00278) | 1950 | 1270 | 4290 | 3810 | 1.13 | 4250 | 1.01 | 1260 | 140 | 4430 | 30.6 |
| | 930† | 591 | 987 | 831 | 1.18 | 929 | 1.06 | 1990 | 94 | 1080 | 10.5 |
| | 420 | 269 | 212 | 172 | 1.23 | 192 | 1.10 | 2130 | 36 | 248 | 5.89 |

* Fig. 2.

† Fig. 1.

these values of H , it is assumed that the average value of B in each annulus occurs at the average radius of the annulus. The error thus introduced is not very serious. The total interior currents thus found have been plotted for each instant of time in terms of the radius of the cylinder. From these curves the current over each of five annuli, each having 1 inch radial depth, has been estimated. Its squared value has been multiplied by the resistance of the annulus, and hence the total C^2R watts at any instant of time have been found. The time-average of the total values has then been taken over a half period of the alternating current. Referring to Table II, it will be seen that at frequency 1/45 (0.0222) the ratio of the watts with alternating to those with continuous current rises to a maximum for a total current of 1000 amperes. In attempting to connect these results with the average permeability of the material, the latter has been found as follows.*

* The time-average of dB/dH has been chosen in preference to the time-average of B/H , because the latter takes no account of the previous history of the material, which is vital when the effects of magnetic hysteresis have to be considered. For example, when the iron is subjected to a periodic magnetising force of fixed direction relative to the iron,

At equal intervals of time the values of the magnetic induction (B) have been taken, and from the hysteresis loops the ratio dB/dH has been found. The time average of dB/dH per coil was then multiplied by the volume of the annulus, and the sum of the averages of the three annuli was divided by the total volume of the cylinder. It will be seen that at frequency $1/45$ the maximum value of this average permeability also occurs with a total current of 1000 amperes. Unfortunately, the ratio of the watts with alternating to those with continuous current at the other frequencies in Table II is not sufficiently large to justify an accurate comparison. All through it is striking how small is the variation of the average permeability. Its value is greatly affected by variation of wave-form. For instance, in fig. 1, where the change of magnetic induction B is rapidly made, the average permeability depends largely upon the maximum value of B . In fig. 2 the change of magnetic induction B gradually takes place over the half period, in which case the average permeability is more dependent upon the intermediate values of B .

(2) The watts due to magnetic hysteresis have been calculated from the area of the hysteresis loops as follows. The maximum values of the magnetic induction (B) over each of the five annuli, corresponding to the maximum values of H obtained from the distribution curves of current have been found. The ergs per cycle per cubic centimetre given by the hysteresis loop corresponding to the maximum value of B have been multiplied by the frequency and the volume of the annulus and by 10^{-7} to reduce to watts. These values have then been added, and the sums are given in Table II. Referring to the experiment at frequency $1/45$, in which the hysteresis watts are 824, the watts which would be dissipated if the distribution under continuous current (rendered non-uniform through end effect) persisted at this frequency are 1170, and if the distribution under continuous current of constant density obtained the watts would have been 1040. This bears out the statement that the watts due to hysteresis for a given total current are diminished by the effect of internal self-induction, commonly referred to as "skin effect."

(3) Using the equation $E = Rx + \frac{dI}{dt}$, where E is the impressed potential difference, R is the ohmic resistance, x the current, and I the total magnetic field external to the annulus considered, it was thought possible to check the values above found by a different process. The value of dI/dt was found

the ratio B/H becomes infinitely great when $H = 0$; whereas the magnetic induction (B) at that moment depends entirely upon the previously applied magnetising forces. This is taken account of in the differential dB/dH , as this is the slope of the curve at the point.

between the surface of the cylinder and the radii 1, 2, 3, and 4 inches respectively, as follows. From the distribution curves of current, and the hysteresis loops, the wave-forms of B were plotted for average radii $1\frac{1}{2}$, $2\frac{1}{2}$, $3\frac{1}{2}$, and $4\frac{1}{2}$ inches. These were then differentiated to find E.M.F.'s, which were multiplied by the area of the annulus considered, and the values for the respective annuli were added together; this gave the value dI/dt . The effect of the magnetic field in the surrounding air space was proved to be negligible. The watts taken by five annuli each $\frac{1}{4}$ inch deep and having average radii of 1, 2, 3, 4, and $4\frac{1}{2}$ inches were found as follows. From the distribution curves the current over each annulus was obtained and thence C^2R ; also the product of the E.M.F. (dI/dt) external to each annulus and the current (x) was found. The sum of these gave at any instant the total watts. The average over a period then followed. Dividing this average by the volume of the annulus the watts per cubic centimetre were obtained at its average radius. A distribution curve was then plotted giving the watts per cubic centimetre in terms of radius, and from this the average watts at radii $\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, $3\frac{1}{2}$, and $4\frac{1}{2}$ inches were obtained. Multiplying these values respectively by the volume of the annulus and adding them together, the total watts were obtained. The hysteresis loss xdI/dt could also be found separately in a similar manner. Three cases have been worked out, and the results are given in Table III, together with the corresponding figures from Table II. This latter method could not be expected to yield such accurate results so far as hysteresis is concerned, since it depends upon the product of an E.M.F. and current largely displaced in phase.

Table III.

| Frequency. | Total maximum current in amperes. | Total watts taken from Table II. | Total watts obtained by alternative method. |
|----------------------|-----------------------------------|----------------------------------|---|
| $1/45$ (0.0222) | 1860 | 5520 | 6110 |
| $1/360$ (0.00278) | 1950 | 4430 | 4460 |
| $1/45$ (0.0222) | 500 | 494 | 480 |

(4) Referring to the ratio of the C^2R and hysteresis watts, it is interesting to note that for a given total current the ratio diminishes as the frequency increases, the increase in the hysteresis watts due to increased frequency much more than counterbalances the decrease, owing to the greater skin

effect. At frequency $1/45$ (0.0222) and maximum total current of 1000 amperes the skin effect is, however, so great (see Table I) as to give a ratio 3.9, not much less than that given by practically the same total current at half the frequency.

Experiments at High Frequency.—The cylinder was transferred to the secondary circuit of a transformer, and various currents up to 1000 amperes were passed through it at a frequency of about 11 periods per second. A dead-beat galvanometer was employed in conjunction with a commutator driven by spur gearing at a speed differing from that of the alternator by 1 part in 10,000, for the purpose of giving the integrals of the curves of E.M.F. of the exploring coils 1, 2, 3. Large E.M.F.'s were, of course, obtained in the case of coil 3, but none in the case of coils 2 and 1. The sensibility of the galvanometer was such that a terminal voltage of 7×10^{-6} could be detected. Table IV summarises the results obtained. It must be borne in mind that, as in the foregoing experiments, the average magnetic induction B is assumed to be effective at the average radius of the coil. On this assumption the total current interior to the radius 4 inches is only from 3 to 5 per cent. of the total current in the cylinder. The actual skin effect is much greater than these figures indicate.

Table IV.

| Frequency. | Total current in amperes. | | Maximum induction B at surface. | Maximum of average induction B through Coil 3. | Current in amperes interior to radius 4 ins. (maximum value). |
|------------|---------------------------|----------|-----------------------------------|--|---|
| | R.M.S. | Maximum. | | | |
| 11.66 | 987 | 1800 | 14,250 | 625 | 56.4 |
| 10.0 | 640 | 1090 | 12,800 | 490 | 47.2 |
| 10.98 | 371 | 691 | 10,200 | 268 | 30.3 |

Application of Results to other Sections.—Comparing two cylinders of the same material whose diameters are as $1:n$, it was shown* that, provided the total currents are as $1:n$ and the frequencies as $n^2:1$, the magnetic forces at similar radii will be the same. It follows also that the total watts due to C^2R and magnetic hysteresis will be the same. Thus, for example, the watts given in Table II refer also to a wire 1 cm. long and 0.1 inch diameter, provided the respective frequencies are 222, 111, 55, and 28, for each of which the total amperes are 5, 10, and 20. The curves in figs. 1 and 2 can also refer to a cylinder 0.1 inch diameter, provided the respective frequencies are 28 and 222, and the total current is 10 amperes, having the

* *Ibid.*

same wave-form. Cylinders having other diameters could be dealt with in the same way.

[*Note added February 22, 1908.*—Lord Rayleigh,* experimenting upon a hard Swedish iron wire 0.16 cm. diameter, found that the ratio of the resistance with alternating to that with continuous currents was about 1.2 when the frequency of the alternating currents was 1050. On the above assumptions this would correspond with a frequency of 0.04 in the case of the cylinder 10 inches in diameter. Table II shows that at frequency 0.022 and 299 R.M.S. amperes the ratio of the resistances is 1.37. Having regard to the fact that the specific resistances and the magnetic qualities of the materials of the two cylinders may have been different, and to the probability that the current in Lord Rayleigh's experiments was less than 1.9 amperes, which is the current corresponding to 299 amperes in the 10-inch cylinder (thereby giving rise to a smaller average permeability), the difference in the ratio of resistances corresponding to given frequencies may be accounted for.]

In conclusion, I wish to thank Mr. Alexander Siemens for the loan of the dynamo used in these experiments. I also wish to acknowledge the help I have received from Mr. A. E. O'dell and Mr. G. F. O'dell. Mr. Robertson, Mr. Franks, and some of my senior students gave me valuable assistance in the experimental part of the work, for which I wish to express my thanks.

* 'Phil. Mag.,' 1886.

*The Effect of Hydrogen on the Discharge of Negative Electricity
from Hot Platinum.*

By Professor H. A. WILSON, F.R.S., King's College, London.

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(Abstract.)

The effect of hydrogen on the discharge of negative electricity from hot platinum was examined by the writer in 1903;* it was found to produce a very large increase in the current. The experiments were all done with nearly new platinum wires which had not been heated in the gas for any great length of time, because it was known that long-continued heating causes the wire to disintegrate. The present paper contains an account of a series of experiments in which wires were heated for long periods in hydrogen, so that any changes in the effect of the hydrogen could be observed. It appears that continued heating in hydrogen alters the character of the effects observed so that the behaviour of an old wire may be very different from that of a new one.

The following gives a short abstract of each section of the paper:—

1. Assuming that $x = Bp^n$, where x denotes the current per square centimetre of platinum at constant temperature, p is the pressure of the hydrogen, and B and n are quantities depending only on the temperature, and also that $x = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$, where θ denotes the absolute temperature and A and Q depend only on the pressure; it is proved that: (1) $n = x\theta^{-1} - c$, where α and c are constants; (2) $Q = P - 2\alpha \log p$; and (3) $A = Kp^{-c}$. These equations are shown to agree with the observations.

Eliminating p from (2) and (3) gives $A = Ke^{(Q-P)c/2\alpha}$. It is shown that all the values of A and Q for new wires satisfy this relation, including those for wires in air. The equation (3) is therefore modified to $A = A_0/(1 + ap^c)$, where A_0 , equal to $K/(1 + \alpha)$, is the value of A in air or when $p = 0$. This equation represents all the values of A . With (4) this gives

$$Q = Q_0 - 2\alpha c^{-1} \log(1 + ap^c).$$

The equation $x = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$ may now be written

$$x = A_0(1 + ap^c)^{(\alpha/c - 1)} \theta^{\frac{1}{2}} e^{-Q_0/2\theta}.$$

If $R = Q_0 + 2(\theta - \alpha c^{-1}) \log(1 + ap^c)$, then $x = A_0\theta^{\frac{1}{2}}e^{-R/2\theta}$, so that the effect of hydrogen can be represented by supposing that it changes Q without altering A .

* 'Phil. Trans.,' A, vol. 202, 1903, p. 352.

If $D = A_0 (1 + ap^c)^{(a/\theta c - 1)}$, then $x = D\theta^{\frac{1}{2}} e^{-Q_0/2\theta}$, so that the effect of hydrogen can be represented by supposing that it changes A without altering Q .

These formulæ are shown to be in agreement with observations by different observers over a very wide range of temperature and pressure.

Assuming that the effect of the hydrogen is due to its presence in the surface layer of the platinum, the conclusion is drawn that the hydrogen in new wires is dissolved in the platinum. The agreement between the formulæ obtained and the observations shows that the equation $x = Bp^n$ which was assumed at the start is correct.

2. It is shown that the leak from a wire which has been heated in hydrogen at a high pressure for some time is nearly independent of the pressure at constant temperature between 0 and 200 mm. of mercury. The conclusion is drawn that the wire contains hydrogen in a state of stable chemical combination, and some experiments are described which seem to support this view.

3. The variation of the leak with the temperature, from a wire giving a leak independent of the pressure, is measured, and Q is found to be 135,000 and A to be 1.67×10^{10} . These values do not satisfy the relation $A = Ke^{(Q-P)/2a}$ which agrees with all the values of A and Q for new wires. On heating the wire in air, and then again in hydrogen at a small pressure, it is found to give the same leak as a new wire in hydrogen; but the leak takes a longer time than before to get to its final value after the pressure has been changed. The conclusion is drawn that heating in hydrogen at a high pressure produces a permanent change in the state of the platinum, which is not removed by heating in air, and which causes the hydrogen to dissolve more slowly in the platinum, but does not affect the final value of the leak. The leak in air is about the same at high temperatures as with a new wire.

4. It is shown that a wire which has been heated in hydrogen at a high pressure, and then in air, on heating in hydrogen at 1600°C . gives the same leak as in air. But at lower temperatures the leak after a time rises to the usual value in hydrogen, and is then large at 1600°C . also. The conclusion is drawn that the wire does not absorb hydrogen above 1600°C . If the temperature is raised when the leak has only partially recovered from its initial very small value, then it falls on raising the temperature and rises again on lowering it.

5. It is shown that the resistance of the wire is slightly increased when it absorbs hydrogen. A wire giving a large leak independent of the pressure was heated for some hours in a good vacuum, and then on heating in air the resistance fell slightly. The conclusion is drawn that the wire still contained

hydrogen. Reasons are given for believing that the stable compound only exists in the surface layer of the platinum.

6. In this section it is shown that the recovery of the leak described in Section 4 can be accelerated by passing an ordinary discharge through the gas from the wire to a neighbouring electrode.

7. The negative leak in hydrogen is compared with the positive leak in oxygen, and it is shown that there is a close analogy between them.

The conclusion is drawn that the negative leak is produced by hydrogen in the same way that the positive leak is produced by oxygen.

In the absence of hydrogen there is, however, a small negative leak due to the platinum alone.

8. In this section it is shown that if the true value of A in the formula $x = A\theta^{1/2}e^{-Q/2\theta}$ is denoted by D , and if D is supposed to be unaffected by the hydrogen, then the true value of Q is given by the equation

$$R = Q + 2\theta \log (D/A).$$

It is shown that the variation of the negative leak from lime with the temperature, as measured by Dr. Horton, is not really inconsistent with the view that D is proportional to the number of free electrons per cubic centimetre of lime.

9. This section contains a theory of the variation of R with the temperature. It is assumed that there is an electrical double layer at the surface of the platinum, and that the electric force in this layer is increased by the presence of electrons in it between the two layers. The increase due to this cause is shown to be greater at higher temperatures. It is shown that

$$R = Nw/J + 4\pi N\rho_0 e^2 t^3 \beta_0^2 \theta^2 / Jw^2,$$

where w is $4\pi\sigma t$, σ is charge per unit area in the layers, and t is distance between the layers. This gives

$$Q^2 \log (D/A) = 4\pi N^3 e^3 \rho_0 t^2 \beta_0^2 \theta / J^3.$$

It is found that a value for D can be obtained which makes $Q^2 \log D/A$ nearly constant. This is explained by supposing that the hydrogen atoms in the platinum are positively charged, and act by neutralising some of the negative charge in the double layer without altering t .

Adopting this value of D as the true value, t is found to be 2.6×10^{-8} cm., which agrees with the thickness of the double layer on platinum polarised by hydrogen in dilute sulphuric acid. The charge carried by the free electrons in 1 c.c. of the platinum is found to be -2.73×10^{14} electrostatic units, which shows that there are eight free electrons to each atom of platinum.

382 *Effect of Hydrogen on Discharge of Negative Electricity.*

This agrees with the fact that platinum is an octovalent element. The values found for R are the following :—

| Gas. | Pressure. | R. |
|----------------------|-----------|--------------------------|
| | mm. | |
| Air | — | 145,000 + 9·68 θ |
| H ₂ | 0·0013 | 110,000 + 19·15 θ |
| H ₂ | 0·112 | 90,000 + 25·14 θ |
| H ₂ | 133 | 56,000 + 36·18 θ |

The value of D adopted is $1\cdot44 \times 10^{10}$, but this may be in error by a factor of 10 or more.

Conclusion.

The view taken in this paper is that the effect of the hydrogen on the leak is due to its presence in the surface layer of the platinum. To explain this it is supposed that the hydrogen atoms in the layer are positively charged, so that they diminish the charge per unit area in the electrical double layer covering the surface of the platinum. The hydrogen appears to dissolve in the platinum at first, but at high pressures in time forms a stable combination with the platinum, having a very small dissociation pressure. Before this compound has been formed, the leak is proportional to a power of the pressure of the hydrogen.

*Comparison of the Board of Trade Ampere-Standard Balance
with the Ayrton-Jones Current-Weigher; with an Appendix
on the Electromotive Forces of Standard Cells.*

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(Received March 10,—Read March 26, 1908.)

When the Board of Trade ampere balance was set up and verified in 1894, the platinum weight (marked A) used with the instrument was adjusted so that a current which deposited silver from a 15-per-cent. solution of silver nitrate at the rate of 1.118 milligrammes per second produced, on reversal, change of force equal to the weight of A. At that period such a current was believed to represent *the ampere*, viz., $1/10$ of a C.G.S. unit, with a fair degree of accuracy.

During the last few years a new current weigher, designed at the Central Technical College,* has been constructed at the National Physical Laboratory with a precision previously not obtained in any instrument for the absolute determination of current strength, and by means of it the electrochemical equivalent of silver† has been determined to a very high degree of accuracy. We therefore considered it of interest to determine the difference between the units of current as measured by the two balances, and at the same time ascertain how nearly the ampere, as measured by the Board of Trade balance, deposits silver at the rate of 1.118 milligrammes per second.‡

The comparison of the two balances was carried out by the aid of cadmium cells and resistances used as secondary standards of current; for example, if current be passed through a resistance, and the strength of the current adjusted until the potential difference between the terminals of the resistance is equal to the E.M.F. of a standard cell, then, when the cell and coil are at given temperatures, a perfectly definite current must be passing through the coil. If this current be determined in absolute measure by means of a current weigher, such as described in the paper previously mentioned, the

* "A New Current Weigher and a Determination of the Electromotive Force of the Normal Cadmium Cell," by Professor W. E. Ayrton, F.R.S., T. Mather, F.R.S., and F. E. Smith, A.R.C.S., 'Phil. Trans.,' A, vol. 207, pp. 463—544.

† "The Silver Voltameter," by F. E. Smith, A.R.C.S., T. Mather, F.R.S., and M. Lowry, D.Sc., 'Phil. Trans.,' A, vol. 207, pp. 545—599.

‡ We may here remark that the official limit of accuracy applied to the Board of Trade standard of current (not to the instrument) is one-tenth part of 1 per cent. See order in Council, 1894.

combination of cell and coil is standardised, and can be used subsequently as a secondary standard of current. Knowing the relations between E.M.F. and temperature for the cell, and between resistance and temperature for the coil, the current required to produce equality of P.D. and E.M.F. at any given temperatures can be found. The combination of cell and resistance can, therefore, be used as a secondary standard of current, at temperatures other than those at which they were standardised.

A set of five cadmium cells set up at the National Physical Laboratory was connected in parallel and used as one cell in the measurements, a sixth cell in the same oil bath being employed in making the preliminary adjustments of current strength.

The principal resistance coil used in the tests was a 1-ohm standard, marked L. 87, which was employed in the determination of the E.M.F. of the Normal Weston Cadmium Cell.* Two other coils, each 0.01 ohm (nominal), were also made use of in some of the comparisons. All three coils have potential terminals. The resistances were measured to a high degree of accuracy at the National Physical Laboratory; their values in international ohms, and those of their current leads and copper blocks with mercury cups for connecting the coils in series, are given in Table I.

Table I.—Values of Resistances employed (International Ohms at 17° C.).

| | |
|---|-------------------------|
| Coil No. L. 87 (between potential terminals)..... | 1.00020 ₂ |
| " 2200 " | 0.010004 |
| " 2492 " | 0.010001 |
| Current leads of L. 87 + two half blocks (mercury cups) | 0.00013 ₄ |
| One current lead of No. 2200 + one half block (mercury cups) | 0.00004 ₈ |
| " " " 2492 + " " " | 0.00004 ₄ |
| Sum of the above | 1.02043 ₁ |
| Temperature coefficient (° C.) of coil L. 87 | + 0.00001 ₉ |
| " " " No. 2200 | + 0.00000 ₈₅ |
| " " " No. 2492 | + 0.00001 ₀₅ |

After standardising the combination of cells and resistance by means of the Ayrton-Jones current weigher at Bushy, they were taken by hand to the Board of Trade Laboratory at Whitehall, and set up in a circuit including the Board of Trade balance. Previous to making any measurements the insulation of the apparatus from earth, and that between the stranded wires connecting the balances and resistances, were tested, and found to be quite satisfactory.

* 'Phil. Trans.,' A, vol. 207, p. 520.

Two methods of comparison were made use of. In one of these, represented by fig. 1, a current (about 1·019 amperes)* sufficient to give a P.D. between the ends

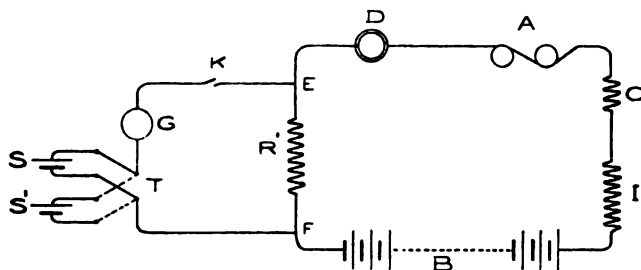


FIG. 1.

D indicates the Board of Trade balance, A the auxiliary Kelvin balance used with D, C adjustable carbon resistances, I iron wire ballast resistances, B a battery of 64 accumulators, R' a standard 1-ohm resistance coil L. 87, S a set of 5 cadmium cells in parallel, S' an auxiliary cadmium cell, T a switch for connecting either S or S' in circuit, G a galvanometer and K a key, E and F are the potential terminals of R'.

of the 1-ohm coil, L. 87, equal to the E.M.F. of the cadmium cell, was passed through the circuit. Additional weights, calculated approximately from the known value of this current, and the known mass of the platinum-iridium weight A, used with the balance, were added to the standard weights, so that the suspended coil would come near the sighted position when the correct current was flowing. The current was then adjusted so as to give exact balance on the galvanometer G, fig. 1, and the rest-point of the balance determined by the vibration method. The current through the fixed coils of the balance was then reversed, readjusted, and the rest-point of the balance again determined. From the two rest-points thus found, and the known sensibility of the instrument, the mass required to balance the change of force on reversal was calculated. The square root of the ratio

$$\frac{\text{Balancing mass}}{\text{Mass of weight A}} \dagger$$

gives the value of the current in Board of Trade amperes.

In the other method of comparison the Board of Trade balance was used in the normal way, without any additional weights, the current being adjusted to 1 Board of Trade ampere approximately, as in ordinary verification tests. This current passed through the standard resistances r , r' , R' , arranged as shown in fig. 2, and the resistance box R, shunting the potential

* The value used in standardising the combination of cells and coils.

† The masses of the weights used were determined to a high order of accuracy by the Office of Standard Weights and Measures, for which we tender our best thanks.

terminals of R' , was adjusted until the P.D. between the points H and J equalled the E.M.F. of the standard cell S. When this condition exists, the

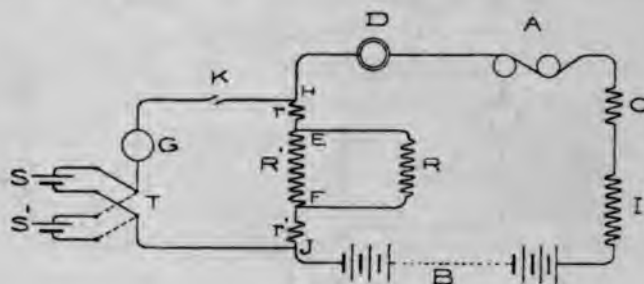


FIG. 2.

The letters have the same meaning as in fig. 1. In addition, H and J are the outer potential terminals of two coils, r and r' , of 0.01 ohm each, and R indicates a box of manganin resistance coils shunting R' .

current through the circuit, in terms of the Ayrton-Jones balance, is given by the formula

$$A = E \left/ \left(r + r' + \frac{RR'}{R + R'} \right) \right.,$$

which, since $R' = 1$, very nearly, may be written

$$A = E \left/ \left(r + r' + R' - \frac{1}{R + 1} \right) \right.,$$

where E is the known E.M.F. of the cell, and $r + r' + R'$ the resistance of the three coils and the contact blocks and current leads included between the points H and J.

To obtain checks on the constancy of the cells and coils the combination was standardised by the Ayrton-Jones balance at Bushy on each of the three days, January 6, 7, and 8, on which comparisons were made at Whitehall; this procedure, in effect, made it unnecessary to know either E.M.F. or resistance in absolute measure, as the ratio only is required, and this was determined directly by the current weigher.

The results of the tests are given in Table II. From this it will be seen that the currents, as measured by the Board of Trade balance, are approximately 0.03₃ per cent. higher than their values in terms of the Ayrton-Jones balance. *The Board of Trade ampere is therefore about 1/30 per cent. smaller than 1/10 of the C.G.S. unit of current as realised by the Ayrton-Jones current weigher.* A difference of this order of magnitude was anticipated by the authors, for the new determination of the electrochemical equivalent of silver, previously referred to,* gives 1.11827 milligrammes of silver per

* 'Phil. Trans.,' A, vol. 207, p. 579.

coulomb, whereas the Board of Trade ampere was intended to be such as would deposit 1.118 milligrammes per second.

Table II.

| No. of experiment. | Date. | Method used. | Value of R (average). | Current as measured by | | Percentage difference. |
|--------------------|----------|--------------------|-----------------------|-------------------------|-----------------------|------------------------|
| | | | | Board of Trade balance. | Ayrton-Jones balance. | |
| 1 | 6. 1. 08 | Added weights | — | 1.0186 ₁ | 1.01836 | 0.02 ₁ |
| 2 | 7. 1. 08 | | — | 1.0188 ₃ | 1.01838 | 0.04 ₁ |
| 3 | 8. 1. 08 | 1-ohm coil shunted | 632 | 1.0000 | 0.99970 | 0.03 ₀ |
| 4 | | | 633 | 1.0000 ₆ | 0.99973 | 0.03 ₃ |
| 5 | | | 730 | 0.9998 ₇ | 0.99951 | 0.03 ₆ |
| 6 | | | 696 | 0.9998 ₆ | 0.99956 | 0.02 ₉ |

Average of 1 and 2 = 0.03₁
 „ 3, 4, 5, and 6..... = 0.03₂.

The percentage difference between the two numbers 1.11827 and 1.118 is 0.02₁, and this differs from 0.03₃ per cent. by 0.00₉ per cent., or less than 1 part in 10,000. *We, therefore, conclude that the Board of Trade ampere is equal to the international ampere, as defined by silver deposit, within 1 part in 10,000, i.e., within 1/100 part of 1 per cent.*

This result is highly satisfactory, seeing that the instrument was set up about 14 years ago. It reflects great credit on the gentlemen responsible for the adjustment, and shows that the care and skill with which the work was carried out was of a very high order. The very close agreement also supplies evidence in favour of the constancy of instruments of this class, and confirms the decision arrived at by the Committee of 1891—94,* that the principle of the balance was the best one to employ. It also gives support to the opinions of Professor Ayrton and the authors, formed after an extensive experience with the Ayrton-Jones balance, that *current weighers properly designed and constructed are the most satisfactory standards of current.*

It is interesting to notice that according to these experiments the Board of Trade ampere will deposit silver at the rate of 1.11827/1.0003₃, i.e., 1.1179₁ milligrammes per second, a value which is nearly identical with the

* This Committee consisted of Sir Courtenay Boyle, Mr. Francis J. S. Hopwood, and Major P. Cardew, representing the Board of Trade; Mr. Preece and Mr. Graves, representing the Postal Telegraph Department; Lord Kelvin and Lord Rayleigh, the Royal Society; Professor Carey Foster and Mr. R. T. Glazebrook, the British Association; and Dr. J. Hopkinson and Professor W. E. Ayrton, the Institution of Electrical Engineers.

number 1·1179₄ given by Lord Rayleigh and Mrs. Sidgwick in their classical memoir of 1884.

We desire to express our hearty thanks to Mr. A. P. Trotter, Electrical Adviser to the Board of Trade, for permitting us to make the comparisons, and also for the valuable help he and Mr. Rennie rendered during the experiments. We are also indebted to Professor Ayrton and Dr. Glazebrook for the kind interest they have taken in the work, and the facilities afforded for carrying it out.

Appendix, received March 20, 1908.

In the above communication we have stated the relation between the Board of Trade ampere and the ampere as determined by the Ayrton-Jones balance. This relation, together with the results given in a previous paper on "A New Current Weigher, etc.,"* by Professor Ayrton and ourselves, enable us to deduce the E.M.F.'s of the normal Weston and Clark cells in terms of the Board of Trade ampere and the Board of Trade ohm. In the last-mentioned paper we have shown that the E.M.F. of the normal cadmium cell, in terms of the ampere as given by the Ayrton-Jones balance and the international ohm as realised at the National Physical Laboratory, is 1·01830 at 17° C., and for the normal Clark cell the value is 1·432₃ at 15° C.

Now, a comparison of resistances made by one of us (F. E. S.), in 1903, gave the following relation:—

$$1 \text{ N.P.L. international ohm} = 1·0001_5 \dagger \text{ Board of Trade ohms ;}$$

and, as above,

$$1 \text{ Ayrton-Jones ampere} = 1·0003_3 \text{ Board of Trade amperes.}$$

The ratio between the values of $C \times R$ is therefore

$$1 : 1·0001_5 \times 1·0003_3,$$

$$\text{i.e., } 1 : 1·0004_8;$$

hence we find that the E.M.F. of the normal Weston cell is

$$\begin{aligned} & 1·01830 \times 1·0004_8 \text{ Board of Trade volts,} \ddagger \\ & = 1·0187_9 \text{ Board of Trade volts at } 17^\circ \text{ C.} \end{aligned}$$

* 'Phil. Trans.,' A, vol. 207, p. 536.

† *Ibid.*, p. 536; also B.A. Report, 1903, pp. 43—4.

‡ The Board of Trade volt being defined as the P.D. between the terminals of a resistance of 1 Board of Trade ohm when a current of 1 Board of Trade ampere is passing through it.

Reducing to 20° C. by the accepted formula, we get

$$\text{E.M.F.} = 1\cdot0186_8 \text{ Board of Trade volts at } 20^\circ \text{ C.}$$

The value published by the Reichsanstalt is 1·0186 volts at the same temperature.

For the normal Clark cell we have

$$\text{E.M.F. in Board of Trade volts} = 1\cdot432_3 \times 1\cdot0004_8 \text{ at } 15^\circ \text{ C.}$$

$$= 1\cdot433_0 \quad ,,$$

This value is in good agreement with the number 1·4329 determined directly by Mr. Trotter at the Board of Trade laboratory in 1904.*

It is gratifying to find such a close approximation between the results obtained in the two distinct ways.

* 'Inst. Elec. Eng. Journ.,' vol. 35, p. 19, 1905; also 'Electrician,' vol. 53, p. 916, Sept. 23, 1904. Mr. Trotter writes, 20/3/08, saying, "Subsequent recalculation of the figures makes the figure 1·4329 preferable to 1·4328, published in the 'Electrician.'"

The Refractive Index and Dispersion of Light in Argon and Helium.

By W. BURTON, B.A., B.Sc., Research Student, formerly Scholar, of Emmanuel College, Cambridge.

(Communicated by Professor J. J. Thomson, F.R.S. Received January 14,—
Read January 30, 1908.)

The initial object of this research was to find the dispersion of light in the monatomic gases argon and helium, but as it was necessary to know the absolute value of the refractive index with considerable accuracy, determinations of the refractive index have also been made. Their relative refractive powers (air = 1) have been found by Rayleigh,* and Ramsay and Travers,† using coloured interference fringes, but no determinations of the absolute refractive index for light of given wave-length have hitherto been made.

The interferometer method due to Jamin was used. A horizontal beam of parallel white light was incident on the first Jamin plate. The two reflected beams traversed two brass tubes of equal length closed by equal thicknesses of worked plane glass. Each brass tube had a small side tube attached which led to apparatus for altering the density in the tube and measuring its pressure. After reflection at the second Jamin plate, the recombined beam was focussed on the slit of a spectrometer, the spectrum obtained with a plane diffraction grating was examined through the telescope of the spectrometer and was seen crossed by bands of maximum and minimum intensity. At the same time, by means of a small reflecting prism, a portion of the slit was illuminated by the light from a Plücker tube containing hydrogen, helium, and mercury vapour. Thus one observed simultaneously the interference bands and certain standard lines of known wave-length with any one of which the cross wire of the telescope could be brought into coincidence.

Refractive Index.—The refractive index (n_0) of a gas at 0° C. and 760 mm. pressure for light of wave-length λ is given by $n_0 - 1 = (1 + \alpha t) \cdot 76 \cdot \frac{f\lambda}{PL}$, where t° C. is the temperature, α is the coefficient of expansion, f is the number of bands which move over the standard line of wave-length λ as the pressure changes by P cm., and L is the length of gas path in the tube.

The values of λ and L are determined once for all, and those of f , P , t are

* Rayleigh, 'Roy. Soc. Proc.,' vol. 59, p. 203.

† Ramsay and Travers, 'Roy. Soc. Proc.,' vol. 64, p. 190, and vol. 67, p. 331.

observed in each experiment as described below. The gas laws are assumed to hold for argon and helium over the limited ranges of pressure and temperature used, and α is taken as equal to 0.00367.

Dispersion.—

Let λ and λ' be the wave-lengths of two standard lines,

n and n' the corresponding refractive indices under pressure H ,

n_1 and n_1' the corresponding refractive indices under pressure H_1 ,

δ the diminution in number of fringes between the standard lines when the pressure changes from H to a less pressure H_1 .

If f be the number of bands crossing λ , then $f + \delta$ is the number of bands crossing λ' , so that the difference of path introduced is

$$(n - n_1)L = f\lambda,$$

and

$$(n' - n_1')L = (f + \delta)\lambda'.$$

Thus

$$\frac{n' - n_1'}{n - n_1} = \left(1 + \frac{\delta}{f}\right) \frac{\lambda'}{\lambda}.$$

Also, from Gladstone and Dale's law,

$$\frac{n - 1}{H} = \frac{n_1 - 1}{H_1} = \frac{n - n_1}{H - H_1},$$

$$\frac{n' - 1}{H} = \frac{n_1' - 1}{H_1} = \frac{n' - n_1'}{H - H_1}$$

Substituting for $(n - n_1)$ and $(n' - n_1')$, we get

$$\frac{n' - n}{n - 1} = \left(1 + \frac{\delta}{f}\right) \frac{\lambda'}{\lambda} - 1.$$

Again, from Cauchy's equation,

$$(n - 1) = a \left(1 + \frac{b}{\lambda^2}\right),$$

we obtain

$$\frac{n' - n}{n - 1} = \frac{b \left(\frac{1}{\lambda'^2} - \frac{1}{\lambda^2}\right)}{1 + \frac{b}{\lambda^2}}.$$

Equating these values, we get

$$b = \lambda^2 \left\{ \left(1 + \frac{\delta}{f}\right) \frac{\lambda'}{\lambda} - 1 \right\} / \left\{ \frac{\lambda^2}{\lambda'^2} - \left(1 + \frac{\delta}{f}\right) \frac{\lambda'}{\lambda} \right\}.$$

The quantities to be determined are λ , λ' , δ and f .

The two former are known, and the latter are observed as described below.

If the absolute value of the refractive index n be known for any wave-length λ , then by substituting for n , λ and b , we determine a in Cauchy's equation.

Experimental Details.—The optical apparatus used is shown diagrammatically in fig. 1. The straight filament of a Nernst lamp was used as a source of light. The lamp was mounted in a collimator tube so that the filament was vertical and at the focus of the collimating lens. The portion of the filament used was limited by a small circular diaphragm of about 2 mm. diameter.

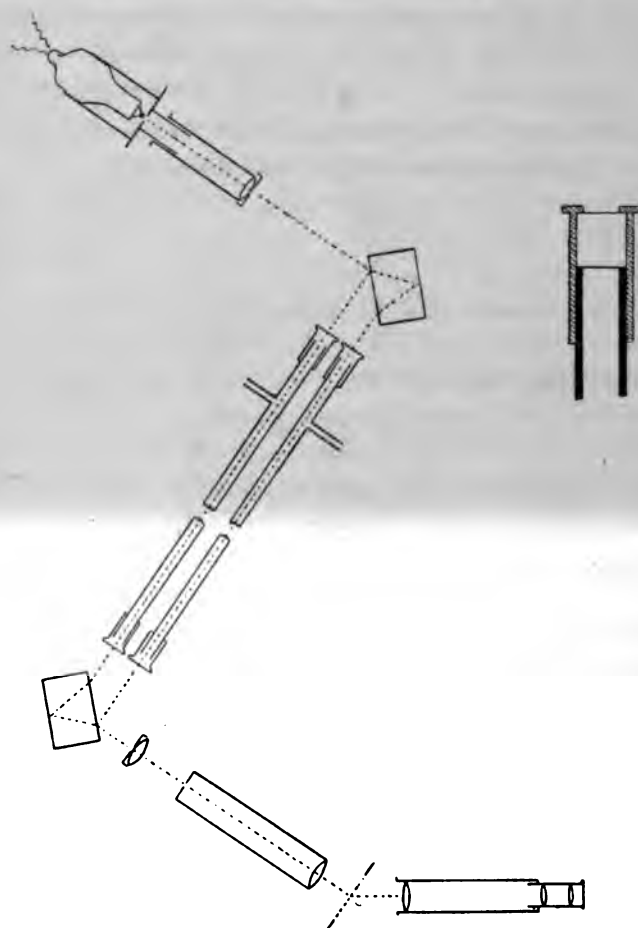


FIG. 1.

placed quite close to it. The collimating tube was supported on an adjustable stand, so that one could thus get a parallel horizontal beam of white light. The brass tube in which the Nernst lamp was mounted was perforated in the neighbourhood of the filament with a ring of holes about 1 cm. in diameter, so that the collimator tube should not get too hot: and radiation from it was prevented from reaching the optical tubes by screens of tin.

Interferometer.—The dimensions of the Jamin plates were $6 \times 4 \times 3$ cm., reflecting surfaces being 6×3 cm. After silvering the back reflecting face of each plate, each was placed on an adjustable screw stand at a convenient distance apart, so that two horizontal parallel beams of white light crossed between them.

The brass tubes to contain the gases were mounted in shallow grooves on adjustable wooden support, and so placed that one of the reflected beams passed through each tube. The tubes were wrapped in cotton wool, and a thermometer reading to tenths of a degree lay between them. The tubes were 109.95 cm. long and about 0.8 cm. internal diameter. They were closed at each end by worked pieces of plane glass, 1 cm. thick, attached by means of cement. These glass ends were held in place by perforated screw caps cemented in position, so that the tubes were capable of standing a considerable internal pressure. Into each tube a smaller side tube was screwed and soldered, for attachment to the apparatus for altering the pressure. The glass and plane glass ends were obtained from Messrs. Adam Hilger and Co. The recombined beam was focussed on the slit of a spectrometer by means of a lens of short focal length. The stands supporting the above, and the source of light, were all on a heavy slate slab built upon brick supports on the middle floor of the laboratory. The apparatus was thus free from vibration and consequent displacement of fringes.

The Analysing Apparatus.—The image of the filament produced by the 5-inch focus lens on the slit of the spectrometer covers only about 1 mm. of the central portion of the length of the slit, so that the spectrum observed, though a plane diffraction grating in the usual way, is narrow in a vertical direction and is crossed by bands. By adjusting one of the Jamin plates the bands can be obtained vertical and at a convenient distance apart. This adjustment is most conveniently made in the first place with a sodium flame source. By altering the width of the slit, the minima can be made more or less black, and there is a cross wire in the eye-piece of the telescope which can be brought into coincidence with the middle of any one of these dark bands.

Standard Lines in the Spectrum.—These were obtained from a small Plücker tube containing hydrogen, helium, and mercury vapour. By the use of a small reflecting prism a portion of the slit was illuminated by the light from the narrow part of the Plücker tube, when certain well-defined lines of known wave-length could be observed. The lines used were five in number, evenly distributed across the visible spectrum. That there was no measurable error introduced by this means of illumination was shown by using at the same time another similar tube placed directly in front of the slit, when the

lines seen were continuous. The standard lines used were the hydrogen red (6.563×10^{-5} cm.), helium yellow (5.876×10^{-5} cm.), mercury green (5.461×10^{-5} cm.), helium green (5.016×10^{-5} cm.), and hydrogen blue (4.861×10^{-5} cm.).

In determining the absolute refractive index, the sodium D_1 line (5.896×10^{-5} cm.) was used, the slit being illuminated directly by a sodium flame, whilst the cross wire was fixed in coincidence with the D_1 line.

Pressure Measurement.—With the tubes used, a change of pressure of 1 atmosphere may cause the transit of about 500 bands in the case of argon, and of about 60 bands in the case of helium. Hence if one wishes to get 300 bands by in the latter case there must be a pressure range of 5 atmospheres, whilst in the former case a range of $\frac{3}{5}$ of an atmosphere will suffice. It was necessary therefore to adopt different methods for altering the pressure in the two tubes.

Argon.—The apparatus used in the case of argon was essentially the same as that adopted by Rayleigh,* for comparing refractivities. It is shown diagrammatically in fig. 2, and the method of changing and measuring the

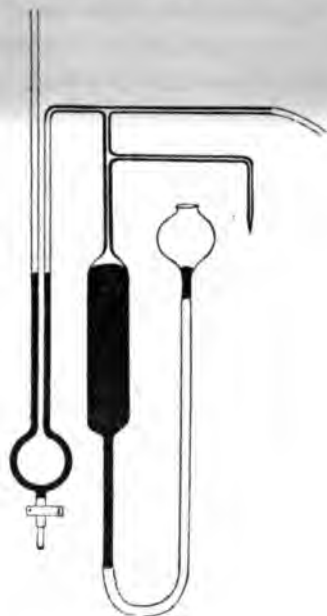


FIG. 2.

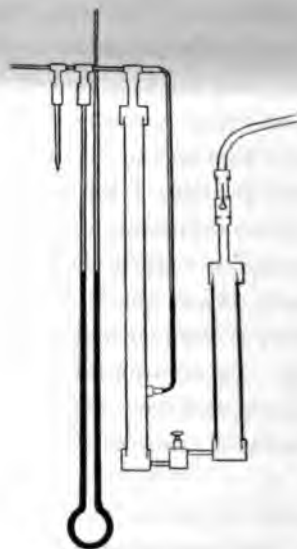


FIG. 3.

pressure is obvious. The reservoir is of about 500 c.c. capacity, and the manometer limbs of 5 mm. diameter. The reservoir is joined to the optical tubes by compo tubing of 4 mm. bore. This tubing is soldered to the side

* Rayleigh, 'Roy. Soc. Proc.,' vol. 59, p. 203.

tube of the optical tube, and fastened by sealing wax to the glass tubing leading from the reservoir. Except for the gauge tubing and the end into which the compo tubing is sealed, all the glass tubing is of capillary bore. This, of course, is used to get the maximum pressure change from a given volume (100 c.c. *q.p.*) of gas. The reservoir and optical tube could be exhausted from the side tube, and through this side tube also the gas could be introduced. After the gas is put in, the side tube is sealed off at a constricted part. The pressure was read on a cardboard millimetre scale placed behind the manometer tubes. This scale was glued on to the wooden support and was afterwards tested against a standard brass scale. Over the range of pressure that was to be used, the scale readings were accurate to well within 1/10 mm. Readings were taken on the scale by eye to 1/10 mm. after a rise in both limbs of the manometer had been caused by constricting the pressure tubing below the gauge. Three such readings at least were taken, and the mean value used.

Helium.—The method of changing and measuring the pressure will be seen from an inspection of fig. 3. The longer reservoir, about 105 cm. long and 11 sq. cm. cross section, is connected above with the pressure and indicator gauges, and through compo tubing with the optical tube. Below it is connected through a steel tap with a shorter cylindrical reservoir about 55 cm. long and 18½ sq. cm. in cross section. As much mercury is introduced as will fill the longer reservoir, and about 10 cm. in length of the shorter reservoir. This leaves about 660 c.c. in the longer reservoir to be occupied by the gas at atmospheric pressure. The cylindrical reservoirs were made from ordinary iron steam piping, and the smaller tubing with which mercury would come in contact was of steel; all connections were made by screw-in joints and sealing wax, the latter being melted into the hot thread before screwing the tubes into position. Above, where the mercury did not extend, brass T-pieces and tubing were used, and the connections were made by screw-in joints and solder. The glass tubing for gauges was of capillary bore, about 2 mm. diameter, and fastened in position with sealing wax. The internal diameter of the brass or steel tubing into which the glass tubes were fitted was widened for the last 2 or 3 inches, so that the glass tube could just fit in, and so that the end could press up against the ledge formed by the difference in internal diameter. The pressure change was produced by forcing mercury from the shorter reservoir into the longer one. This was done by pumping air into the former. To do this, the valve from a motor tyre was soldered on the top of the shorter reservoir, and a foot pump used for motor tyres enabled a pressure up to 10 atmospheres to be obtained if necessary. The steel tap was then closed

and the valve opened. By turning the steel tap now, and slowly reducing the pressure, it was quite easy to count the bands as they moved as slowly as desired over the cross wire. Whilst taking observations for the refractive index, one limb of the manometer gauge was open. The pressure range then measured was about 1300 mm. Readings were taken by eye on a millimetre cardboard scale placed behind the manometer. It was endeavoured to read to $1/10$ mm., but as the tubing was of capillary bore and the range considerable, this was not always possible, especially at the lower part of the scale. This degree of accuracy is, however, not necessary, for there was only a transit of 100 bands, and if these were read to one-twentieth of the distance between two bands, the error may be 1 in 2000, and, therefore, the pressure readings need only be taken to $\frac{1}{2}$ mm. to obtain a corresponding degree of accuracy. When experiments for the dispersion were made over a wide pressure range, the open limb of the manometer was sealed. The gas laws were assumed to hold for helium, and the pressure change was not measured, the assumption being that for a range of pressure from 1 to 6 atmospheres the same laws held as from 1 to 3 atmospheres. Before introducing any mercury into the apparatus, air was pumped in till the pressure was about 10 atmospheres, and the whole was placed under water, when no leaks could be discovered. Again, after putting mercury into the reservoirs and manometer, it was pumped up, and readings of the pressure taken on successive days. By this method any leaks could usually be detected, but very small leaks might be obscured by the changes due to temperature. The sealing wax joints were satisfactory, and no leaks were observed from them. On one occasion a leak was found from a solder joint, and on another from the compo tubing which led to the optical tube.

Refractive Index and Dispersion of Argon.—The gas was prepared by Sir Wm. Ramsay and obtained from Messrs. Tyrer and Co. It was introduced directly into the apparatus, after the latter had stood exhausted overnight with a phosphorus pentoxide drying bulb and a small Plücker tube attached, the latter showing that there had been no leak. The reservoir being sealed off, the refractive index and dispersion were determined as below. A typical set of readings taken is given in each case, and later the results of all the other readings made are tabulated and the mean is taken.

Refractive Index.—Pressures were read to $1/10$ mm. after causing a rise in both limbs of the manometer, the mean of three such readings at least being taken. The number of bands crossing the standard line was read to one-twentieth of the distance between two bands when possible. As the pressure range used was about 450 mm., and the number of bands about

280, the error in these measurements is probably 1 in 3000. The temperature of the tubes is read to $1/10^\circ$ C., and in no case did the temperature change by more than $1/10^\circ$ C. in the course of an experiment which lasted less than 10 minutes. The temperature of the manometer was also observed. The thermometers had previously been compared with a standard thermometer, and for the range of temperature 16° to 19° C., over which these experiments were made, the thermometers agreed to within $1/10^\circ$ C., so that no connection was necessary for the degree of accuracy aimed at in these determinations. Readings were taken for the refractive index relative to the D_1 line and also to the hydrogen red, as this allowed a check on the accuracy of the measurements, both of the refractive index and of the dispersion.

Dispersion.—The dispersion was found at the same time as the refractive index for the hydrogen red line. The number of fringes between the standard lines was estimated to one-twentieth whenever possible. As the distance apart of the black bands and their breadth vary considerably with the pressure, it is not possible to read with the same degree of accuracy always. The bands were used when as far apart as possible over the pressure range employed. This, of course, is attained by preliminary adjustment of the Jamin plates, and subsequent alteration of pressure in the other optical tube if necessary. The results obtained are given below.

The following is a typical series of experiments:—

Refractive Index of Argon for D_1 line. Tuesday, July 30, 1907.

Time, 3.47. Temperature of tubes, $16^\circ.65$ C. Temperature of manometer, $17^\circ.5$ C.

| Pressure. | | | | | | | |
|-----------|-------|-------|-------|--------|-------|-------|-------------|
| Initial. | | | | Final. | | | Difference. |
| 474.5 | 475.3 | 476.2 | 477.0 | 708 | 709.5 | 710.1 | 494.0 |
| 458.8 | 459.5 | 460.5 | 461.3 | 214 | 215.5 | 216.0 | 15.7 |
| 15.7 | 15.8 | 15.7 | 15.7 | 494 | 494.0 | 494.1 | 478.3 |

Number of bands crossing D_1 line and direction = 313.7, to right.

Time, 3.55. Temperature of tube, $16^\circ.7$ C. Temperature of manometer, 17° C.

Substituting the values below in

$$(n_0 - 1) = (1 + at) \cdot 760 \cdot \frac{f\lambda}{PL},$$

$$a = 0.00367$$

$$t = 16^\circ.7 \text{ C.}$$

$$f = 313.7$$

$$\lambda = 5.896 \times 10^{-8} \text{ cm.}$$

$$P = 478.3 \text{ mm.}$$

$$L = 109.95 \text{ cm.,}$$

we get

$$n_0 = 1.0002837,$$

where n_0 is the refractive index at 0° , 760 mm. pressure, for the D_1 line.

Dispersion in Argon and Refractive Index for H red. Tuesday, July 30, 1907.

Time, 4.4. Temperature of tubes, $16^\circ.7$ C. Temperature of manometer, 17° C.

| Pressure. | | | | | | | | | |
|-----------|-----|-------|-------|--------|-------|-------|-------|-------------|--------|
| Initial. | | | | Final. | | | | Difference. | |
| 710 | 708 | 709.5 | 710.1 | 477 | 477.2 | 474.0 | 474.5 | 475.5 | 494.00 |
| 216 | 214 | 215.5 | 216.0 | 461 | 461.2 | 457.9 | 458.2 | 459.5 | 16.08 |
| 494 | 494 | 494.0 | 494.1 | 16 | 16.0 | 16.1 | 16.3 | 16.0 | 477.92 |

Number of bands crossing H red and direction = 280.95 to left.

Number of Bands between Standard Lines and H red.

| H red. | He yellow. | Hg green. | He green. | H blue. |
|-------------|------------|-----------|-----------|---------|
| Initially 0 | 39.6 | 68.65 | 105.55 | 119.9 |
| 0 | 39.6 | 68.6 | 105.45 | 119.85 |
| Mean 0 | 39.6 | 68.63 | 105.5 | 119.87 |
| Finally 0 | 5.8 | 10.07 | 15.45 | 17.55 |
| 0 | 5.8 | 10.03 | 15.5 | 17.55 |
| Mean 0 | 5.8 | 10.05 | 15.47 | 17.55 |

Time, 4.30. Temperature of tubes, 16° 72 C. Temperature of manometer, 17° 5 C.

This gives $n_0 = 1.0002830$ for the H red line at 0° and 760 mm.; also for δ the diminution in the number of fringes between the H red and the standard lines above, when f bands cross the H red,

we get δ 0 32.8 58.57 90.03 102.32,

whence $(1 + \frac{\delta}{f})$ 0 1.1203 1.2085 1.3205 1.3642.

Results.

Refractive Index of Argon at 0° and 760 mm. for D₁ line.

| Date. | Temperature (t). | Pressure change (P). | No. of bands (f). | n at 0° and 760 mm. |
|-------------------------|------------------|----------------------|-------------------|-----------------------|
| Friday, July 26 | 17.5 | 439.8 | 287.6 | 1.0002836 |
| | 17.6 | 439.4 | 287.2 | 2836 |
| | 17.8 | 438.65 | 286.65 | 2837 |
| Saturday, July 27 | 16.95 | 435.75 | 285.5 | 2836 |
| | 17.05 | 437.03 | 286.4 | 2838 |
| | 17.2 | 242.13 | 158.55 | 2837 |
| Monday, July 29 | 17.8 | 480.0 | 313.5 | 2836 |
| | 17.9 | 479.1 | 312.8 | 2836 |
| | 18.0 | 479.9 | 313.25 | 2836 |
| Tuesday, July 30 | 16.5 | 477.2 | 313.2 | 2837 |
| | 16.63 | 478.35 | 313.65 | 2835 |
| | 16.7 | 478.3 | 313.7 | 2837 |
| Friday, August 9 | 18.75 | 362.2 | 286.0 | 2838 |
| | 18.9 | 565.6 | 368.2 | 2837 |
| | 18.9 | 203.25 | 132.25 | 2837 |
| | | | Mean | 1.0002837 |

Refractive Index of Argon at 0° and 760 mm. for H red.

| Date. | Temperature (t). | Pressure change (P). | No. of bands (f). | n at 0° and 760 mm. |
|------------------|------------------|----------------------|-------------------|---------------------|
| July 26 | 17·92 | 438·45 | 256·7 | 1·0002830 |
| y, July 27 | 17·4 | 480·15 | 281·45 | 2829 |
| | 17·6 | 438·65 | 257·14 | 2830 |
| r, July 29 | 18·1 | 480·0 | 280·65 | 2829 |
| | 18·2 | 479·3 | 280·1 | 2828 |
| r, July 30 | 16·72 | 477·92 | 280·95 | 2830 |
| | 16·75 | 477·4 | 280·54 | 2829 |
| August 9 | 19·0 | 352·9 | 205·8 | 2830 |
| | | | Mean | 1·0002829 |

Dispersion in Argon, $1 + \frac{\delta}{f}$.

| Date. | f. | He yellow. | Hg green. | He green. | H blue. |
|-------------------------------------|--------|------------|-----------|-----------|---------|
| July 26 | 256·7 | 1·1202 | 1·2082 | 1·3204 | 1·3642 |
| y, July 27 | 281·45 | 1·1206 | 1·2085 | 1·3206 | 1·3639 |
| | 257·15 | — | — | — | 1·3642 |
| r, July 29 | 280·65 | 1·1206 | 1·2090 | 1·3207 | 1·3651 |
| | 280·1 | 1·1206 | 1·2086 | 1·3205 | 1·3644 |
| r, July 30 | 280·95 | 1·1203 | 1·2085 | 1·3205 | 1·3642 |
| | 280·54 | 1·1205 | 1·2085 | 1·3206 | 1·3648 |
| August 9 | 205·8 | 1·1206 | 1·2090 | 1·3202 | 1·3645 |
| Mean $(1 + \frac{\delta}{f})$ | | 1·1205 | 1·2086 | 1·3205 | 1·3644 |

nd b we reduce as below, where λ refers to the H red line 10^{-6} cm.), λ' to the other standard lines.

| | He yellow. | Hg green. | He green. | H blue. |
|------------------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| | $5·876 \times 10^{-6}$ cm. | $5·461 \times 10^{-6}$ cm. | $5·016 \times 10^{-6}$ cm. | $4·861 \times 10^{-6}$ cm. |
|) | 1·1205 | 1·2086 | 1·3205 | 1·3644 |
|) $\frac{\lambda'}{\lambda}$ | 1·0082 | 1·0057 | 1·0093 | 1·0106 |
| | 0·0032 | 0·0057 | 0·0093 | 0·0106 |
| | $5·6 \times 10^{-11}$ | $5·6 \times 10^{-11}$ | $5·7 \times 10^{-11}$ | $5·6 \times 10^{-11}$ |

Mean $b = 5·6 \times 10^{-11}$.

$$\begin{aligned}
 &\text{Taking} & (n-1) &= a \left(1 + \frac{b}{\lambda^2} \right), \\
 &\text{and substituting} & b &= 5.6 \times 10^{-11}, \\
 & & n &= 1.0002837 \text{ for } D_1 \text{ line,} \\
 & & \lambda &= 5.896 \times 10^{-5} \text{ cm.,} \\
 &\text{we get} & a &= 0.0002792; \\
 &\text{therefore} & n &= 1.0002792 + \frac{1.6 \times 10^{-14}}{\lambda^2}.
 \end{aligned}$$

Helium.—This was prepared from thorium. The thorium was placed in one half of a porcelain tube, the other half containing copper oxide. The tube was attached to a mercury pump, and through a tube containing solid caustic potash to a gas collector full of boiled caustic potash solution. There was also a mercury gauge to indicate the pressure in the apparatus. After exhausting and shutting off the pump, the porcelain tube was heated in a combustion furnace until the pressure indicated by the manometer was just above atmospheric pressure. Connection with the collecting reservoir was then made, and the gas slowly accumulated in it. In this manner about 1 litre of helium was collected. The thorium being heated at atmospheric pressure, the helium comes off very slowly, but any hydrogen present should, under these conditions, be removed by the red-hot copper oxide. The gas was introduced about 200 c.c. at a time into the exhausted reservoir attached to the optical tube. Before entering the reservoir, the gas was passed through a drying tube of calcium chloride and a tube of charcoal surrounded by liquid air, each portion of the gas being kept in contact with the charcoal for half an hour before being passed on to the reservoir. A Plücker tube attached to the mercury pump, and arranged before the slit of the spectrometer, enabled one to test the gas spectroscopically from time to time. No trace of foreign gases could be observed. After sufficient gas had been introduced to give the required pressure range, the reservoir containing it was sealed off, and the experimental results given below were obtained.

Refractive Index.—The pressure range being 1300 mm., it is not necessary, as stated before, to read to more than $\frac{1}{2}$ mm. to get an accuracy of 1 in 2000, though readings were attempted to 1/10 mm. The number of bands crossing the standard line used was about 100, so that to get the same degree of accuracy it is necessary to read to one-twentieth of the distance between two bands. As it was possible in the case of helium always to start and end with the cross wire coincident with a standard line and with the middle of a black band, I consider this accuracy was obtainable. It may be remarked

here that with gases of small refractive power like helium the accuracy of the value for the refractive index depends largely on the accuracy with which the number of bands that cross the standard line can be estimated; for with the same pressure range in helium only one-eighth the number of bands will cross the same standard line as in the case of air or argon. It will be observed below that the value of the refractive index shows a slight increase from day to day, whilst the values agree well on any single day. This slight increase was, I think, due to a small air leak. If, in the course of the three days over which the experiments were made, an air leak of 1 in 2500 had occurred, the variation observed would be accounted for. The same increase is observed in the value for the H red line, and the same agreement on any one day. That the increase was less from Tuesday to Wednesday afternoon is accounted for by the fact that when the gas was put in I arranged the level of the mercury in the reservoir so that after sealing off and opening the tap connecting the reservoirs the gas should be under pressure slightly greater than atmospheric. The barometer rose on Tuesday night and the temperature fell, so that the observed fall in pressure on Wednesday morning might very possibly have been due to these changes; and that this was largely the case is shown by the results obtained on Wednesday afternoon. The gas, however, was left on Wednesday afternoon under slightly less than atmospheric pressure, and subsequent readings taken at night showed on reduction a decided but small increase in the refractive index. Again on Thursday morning an increase was observable. The values therefore obtained on Tuesday, soon after the gas was put in, and on Wednesday afternoon, are probably most correct. It will be seen that the extreme values for the refractive index obtained during the three days do not differ by more than 1 in 350, so that the readings for the dispersion were not measurably altered by the change in the refractive index. As in the case of argon, measurements of the refractive index for the D_1 line and the H red were made, and a summary of the results is given below.

Dispersion.—In some of the experiments the open limb of the manometer was sealed off, and the pressure change arranged so that about 250 bands crossed the H red line. As in the case of argon, the bands were estimated to one-twentieth when possible, and the fringes used when the bands were as far apart as possible over this pressure range. There is no great advantage in having a larger number of bands than 250 crossing the standard line, for the bands get so close together in the blue and green that it is difficult to measure them accurately, and what is gained in accuracy in the measurement of f is lost in the measurement of δ .

Refractive Index at 0° and 760 mm. for D_1 line.—The observations were

taken and reduced in a similar manner to those of argon, except that the scale reading of the manometer used was the result of one observation only and not the mean of several.

Refractive Index of Helium at 0° and 760 mm. for D₁ line.

| Date. | Temperature (t). | Pressure change (P). | No. of bands (f). | n at 0° and 760 mm. |
|-------------------------------|------------------|----------------------|-------------------|---------------------|
| Tuesday, August 6..... | 18.8 | 1245.9 | 100.1 | 1.00003500 |
| | 18.7 | 1244.5 | 100 | 3499 |
| Wednesday afternoon, August 7 | 16.1 | 1232.7 | 100 | 3501 |
| Wednesday night, August 7 | 16.25 | 1230.8 | 100 | 3509 |
| | 16.25 | 1230.2 | 100 | 3510 |
| | 16.3 | 1230.7 | 100 | 3510 |
| Thursday, August 8 | 17.1 | 1232.7 | 100 | 3514 |
| | 17.2 | 1233.6 | 100 | 3512 |
| | 17.3 | 1233.4 | 100 | 3514 |
| | 17.4 | 1283.9 | 104 | 3512 |

As explained above, the value most probably correct is 1.00003500, the mean of the first three observations.

Refractive Index of Helium at 0° and 760 mm. for H red.

| Date. | Temperature (t). | Pressure change (P). | No. of bands (f). | n at 0° and 760 mm. |
|---------------------------|------------------|----------------------|-------------------|---------------------|
| Tuesday, August 6..... | 18.4 | 1315.6 | 95 | 1.00003497 |
| Wednesday night, August 7 | 16.4 | 1289.9 | 94 | 3505 |
| | 16.4 | 1303.6 | 95 | 3505 |
| Thursday, August 8 | 16.7 | 1357.8 | 99 | 3510 |
| | 16.8 | 1318.5 | 96 | 3507 |
| | 17.0 | 1345.3 | 98 | 3511 |

$$\text{Dispersion in Helium, } 1 + \frac{\delta}{f}.$$

Where the number of bands crossing the H red line was greater than 100, the open limb of the manometer was sealed off and the pressure was not read.

| Date. | f . | He yellow. | Hg green. | He green. | H blue. |
|-----------------------------------|-------|------------|-----------|-----------|---------|
| Wednesday, August 7 | 100 | 1·1185 | 1·2053 | 1·3130 | 1·3560 |
| | 94 | 1·1195 | 1·2055 | 1·3135 | 1·3558 |
| | 95 | 1·1184 | 1·2045 | 1·3137 | 1·3558 |
| Thursday, August 8 ... | 99 | 1·1177 | 1·2040 | 1·3131 | 1·3550 |
| | 96 | 1·1192 | 1·2041 | 1·3125 | |
| | 98 | 1·1179 | 1·2034 | 1·3127 | 1·3551 |
| | 250 | 1·1182 | 1·2046 | 1·3132 | 1·3560 |
| | 101 | 1·1183 | 1·2040 | | |
| | 99 | 1·1177 | 1·2040 | 1·3131 | 1·3565 |
| | 200 | 1·1177 | 1·2040 | 1·3127 | 1·3551 |
| | 250 | 1·1180 | 1·2043 | 1·3132 | 1·3557 |
| | 250 | 1·1186 | 1·2050 | 1·3139 | 1·3566 |
| | 250 | 1·1179 | 1·2041 | 1·3129 | 1·3558 |
| Mean $1 + \frac{\delta}{f}$ | | 1·1183 | 1·2044 | 1·3131 | 1·3557 |

To find b .—Reducing these values as for argon, λ referring to the H red line ($6\cdot563 \times 10^{-5}$ cm.), we get:—

| | He yellow. | Hg green. | He green. | H blue. |
|--|----------------------------|----------------------------|----------------------------|----------------------------|
| λ' in cm. | $5\cdot876 \times 10^{-5}$ | $5\cdot461 \times 10^{-5}$ | $5\cdot016 \times 10^{-5}$ | $4\cdot861 \times 10^{-5}$ |
| $1 + \frac{\delta}{f}$ | 1·1183 | 1·2044 | 1·3131 | 1·3557 |
| $\left(1 + \frac{\delta}{f}\right) \frac{\lambda'}{\lambda}$ | 1·0012 | 1·0022 | 1·0036 | 1·0041 |
| $\frac{n' - n}{n - 1}$ | 0·0012 | 0·0022 | 0·0036 | 0·0041 |
| b | $2\cdot1 \times 10^{-11}$ | $2\cdot1 \times 10^{-11}$ | $2\cdot2 \times 10^{-11}$ | $2\cdot2 \times 10^{-11}$ |

Mean $b = 2\cdot2 \times 10^{-11}$.

Taking $n - 1 = a \left(1 + \frac{b}{\lambda^2}\right),$

and substituting

$$b = 2\cdot2 \times 10^{-11}$$

$$n = 1\cdot00003500 \text{ for } D_1 \text{ line,}$$

$$\lambda = 5\cdot896 \times 10^{-5} \text{ cm.,}$$

we get

$$a = 0\cdot00003478;$$

therefore

$$n = 1\cdot00003478 + \frac{7\cdot6 \times 10^{-16}}{\lambda^2}.$$

Discussion of Results.

Argon.—The value obtained for the refractive index for D₁ line is 1·0002837. Ramsay and Travers* give the refractive power (air = 1) as 0·968 for the brightest part of the spectrum. If air be taken as 1·0002922 for the mean D line (Kayser and Runge†), this makes argon to be 1·0002828. Ramsay and Travers used a pressure range of about 500 mm., corresponding to a transit of between 30 and 40 bands. The pressure range used above is about the same, but corresponds to a transit of nearly 300 bands. The results agree to 1 in 300, and closer agreement can hardly be expected, for if the refractive index of air for the brightest part of the spectrum be taken as 1·000293, the results are practically identical.

The dispersion of argon is slightly less than that of air, if the coefficient b for air be $5·8 \times 10^{-11}$ as found by Mascart.‡

Helium.—The value of the refractive index for the D₁ line is 1·00003500. Ramsay and Travers give the refractive power (air = 1) as 0·1238, and if air be taken as 1·0002922, this gives a value for helium of 1·0000361, which is considerably larger than that obtained above. Assuming that Ramsay and Travers used the same apparatus as for argon, the same pressure range would correspond to a transit of between 4 and 5 bands only in the case of helium. Hence the accuracy of the value of the refractive power will depend largely on the accuracy with which, after a change of pressure, the middle of the movable band can be brought back into continuation with the middle of the fixed band used as a fiducial line. Ramsay and Travers considered that they could estimate to 1/25 of a band, so that the error of the setting may be 1 in 100. The accuracy of their pressure measurements was increased by comparing the refractive power of helium with that of hydrogen, and then that of the latter with air. By this means the bands were kept in position in the field of view over a wider range of pressure than was possible when helium was compared directly with air. The difference in the value obtained by Ramsay and Travers and that obtained above may perhaps be attributed to the fact that the pressure changes in the experiments of the former compensate for the transit of so small a number of bands, though a difference of 3 per cent. in the refractive power is more than one might expect.

The dispersion is, as will be seen, much smaller than that of any other gas so far examined, the coefficient b being almost exactly half that found by Mascart in the case of hydrogen.

* Ramsay and Travers, 'Roy. Soc. Proc.,' vol. 67, p. 331.

† Kayser and Runge, 'Abh. d. Berl. Akad.' (1893).

‡ Mascart, 'Ann. de l'École Normale' (1877).

The results for argon and helium are tabulated below, and, for comparison, Mascart's values for hydrogen are also given.

Refractive Index, reduced to 0° C. and 760 mm. pressure for D₁ line.

| | |
|------------------------|------------|
| Argon | 1·0002837 |
| Helium | 1·00003500 |
| Hydrogen (Mascart)*... | 1·0001387 |

Dispersion :—In equation

$$n-1 = a\left(1 + \frac{b}{\lambda^2}\right), \text{ or } n = A + \frac{B}{\lambda^2},$$

| | <i>b.</i> | <i>a</i> | <i>A.</i> | <i>B.</i> |
|----------------------------|---------------------------|------------|------------|---------------------------|
| Argon..... | $5\cdot6 \times 10^{-11}$ | 0·0002792 | 1·0002792 | $1\cdot6 \times 10^{-15}$ |
| Helium | $2\cdot2 \times 10^{-11}$ | 0·00003478 | 1·00003478 | $7\cdot5 \times 10^{-16}$ |
| Hydrogen ... (Mascart)† | $4\cdot3 \times 10^{-11}$ | 0·0001376 | 1·0001376 | $5\cdot9 \times 10^{-16}$ |

It may be noted that the values of a/b for these substances are approximately in the ratio 3 : 1 : 2.

I wish to thank Professor J. J. Thomson for suggesting this work to me and for the interest he has taken in it. My thanks are also due to Mr. C. T. R. Wilson, to whom I am much indebted for advice in all that pertains to the optical part of this work.

* *Loc. cit.*

† *Loc. cit.*

On the Refractive Indices of Gaseous Nitric Oxide, Sulphur Dioxide, and Sulphur Trioxide.

By C. CUTHBERTSON, Fellow of University College, London, and E. PARR
METCALFE, B.Sc., 1851 Exhibition Scholar.

(Communicated by Professor F. T. Trouton, F.R.S. Received February 11,—
Read February 20, 1908.)

Nitric Oxide.

Dufet only records two determinations of the index of nitric oxide: that of Dulong, who found 1·000302 for white light, and that of Mascart,* who gives, for sodium light, 1·0002975, taking air as 1·0002928. The latter states that the gas he used contained about 10 per cent. of gas not absorbable by ferrous sulphate, for which allowance was made; but the analysis was not very accurate. As the index is abnormally high, and methods of purifying gases have improved since 1877, it seemed desirable to repeat the determination.

A specimen of the gas was kindly lent us by Miss I. Homfray. It was prepared by the method of Van Deventer† and purified by fractionation at low temperatures.

The mean of eight experiments which did not differ by 1 per cent. was, for sodium light,

$$\mu = 1\cdot0002939.$$

Taking the index of oxygen as 1·0002702, and that of nitrogen as 1·0002973, the additive value for NO would be 1·0002837. Hence the index is abnormally large, though not quite so much so as previous determinations had made it. This peculiarity it shares with all other nitrogen compounds whose gaseous index has been determined.

Sulphur Dioxide.

The principal determinations of the index of gaseous sulphur dioxide have been :—

* 'An. de l'Ec. Normale sup.,' vol. 6, p. 1, 1877.

† See R. W. Gray, 'Chem. Soc. Trans.,' 1905, vol. 87, p. 1601.

| Observer. | Wave-length. | $(\mu - 1)10^6$. | Remarks. |
|--------------------------|--------------|-------------------|---|
| Dulong* | White | 662.0 | Reduced to proportion with air = 292.3. |
| Ketteler, 1865 and 1885† | D | 686.0 | Approximate calculation. |
| Ketteler | D | 675.94 | Correct calculation. |
| Mascart, 1874‡ | D | 682.0 | |
| Mascart, 1877§ | D | 702.6 | |
| G. W. Walker | D | 675.8 ± 5 | |

* 'Ann. de Chim. et de Phys.,' vol. 31, p. 154, 1826.

† Ketteler, 'Theor. Optik,' 1885, p. 459.

‡ Mascart, 'C. R.,' vol. 78, pp. 617, 679, 1874.

§ Mascart, 'An. de l'Ec. Normale sup.,' vol. 6, p. 1, 1877.

|| G. W. Walker, 'Phil. Trans.,' vol. 201, p. 435, 1903.

The explanation of these discrepancies is that the object of the experimenters appears to have been to arrive at the index of the gas at 0° C. and 760 mm., and their observations were made at different temperatures and pressures, and reduced by different coefficients. Thus Dulong worked with low pressures, probably not exceeding 340 mm., and does not appear to have made any corrections for deviations from the laws of Boyle and Gay-Lussac. Ketteler calculated his results by two methods: with and without allowance for deviation from Boyle's law. In both cases he used a temperature coefficient of $1 + 0.00411t$. By the second method he obtained the number 686, which is quoted by Dufet.* By the first he arrived at 675.94. His maximum pressure was 1100 mm.

Mascart, in 1874, used a temperature coefficient of $1 + 0.00471t$ and a pressure coefficient of $1 + 0.025p$. His pressures amounted to eight atmospheres. In 1877 he employed $1 + 0.00460t$ and $1 + 0.025p$. He worked at a mean pressure of 1050 mm.

Walker uses a pressure coefficient of $1 + 0.000398p$ and a temperature coefficient of $1 + t(0.00416 \pm 0.00002)$. His mean pressure was about 650 mm.

On the present occasion an attempt was made to measure the index in relation to the density of the gas, so as to show the retardation caused by the same number of molecules per unit volume as exist in hydrogen at normal temperature and pressure. The gas used was obtained from a siphon, and dried by P_2O_5 . Very low pressures were used, the greatest being under 200 mm. A density bulb was put in connection with the refractometer tube and immersed in the same water bath. In each experiment the quantity of SO_2 present was estimated by the observation of pressure and temperature and by the density of the gas.

* Dufet, 'Recueil des Données Numériques,' vol. 1, p. 78.

The following table shows the results obtained:—

| Experiment. | $(\mu-1)10^6$. | |
|---------------------------|--------------------------|-------------------------------|
| | Calculated from density. | Calculated from p and t . |
| 1 | 659·9 | 660·7 |
| 2 | 660·99 | 659·03 |
| 3 | 652·0 | 647·0 |
| 4 | 664·6 | 659·5 |
| 5 | 662·4 | 659·8 |
| Means, omitting No. 3 | 661·97 | 659·76 |
| Mean of two methods | 660·86 | |

The third experiment is out of line with the rest, and should, we think, be neglected. We have been unable to trace the source of error, but, from the fact that it affects both methods, it is probably to be ascribed to a clerical error in recording the data. The agreement between the two methods is satisfactory.

In order to compare this result with those of previous experimenters, it is necessary to multiply their figures by the ratio of the theoretic density of SO_2 to the experimental value.

Taking $\text{O} = 16$, $\text{S} = 32\cdot056$, and the weight of a litre of oxygen as $1\cdot10523$ gr., we find the theoretic density to be $2\cdot2123$ (air = 1); and Leduc* has found experimentally the value $2\cdot2639$. The ratio of these numbers is $0\cdot97722$.

With this correction the different determinations are:—

| | $(\mu-1)10^6$. | |
|------------------------------|-------------------|------------|
| | Uncorrected. | Corrected. |
| Dulong | 662·0 | — |
| Mascart, 1877..... | 702·6 | 686·6 |
| Ketteler | 675·94 | 660·5 |
| Walker | $675\cdot8 \pm 5$ | 660·4 |
| Cuthbertson and Metcalfe ... | — | 660·9 |

Dulong's pressures were so low that the correction would be inappropriate in his case. It is not easy to understand the divergence of Mascart's later

* Leduc, 'Ann. de Ch. et de Phys.,' vol. 15, 1898, p. 94.

value. But we find ourselves in agreement with the determinations of the other two observers, and conclude that they are nearest to the truth.

Sulphur Trioxide.

The compound was prepared by passing dry SO_2 and O_2 over platinised asbestos, and was then introduced into small capillary tubes in suitable quantities and sealed off *in vacuo*. The method used was to place the sealed capillary in the quartz refractometer tube and, when this had been evacuated and sealed off, to break the capillary tube with a jerk. The refractometer tube was then alternately cooled with liquid air and heated in the furnace. The weight of SO_3 was calculated from the difference between the original tube filled with the solid and the glass fragments collected after the experiment. The figures were checked by titration of the SO_3 , and by precipitation with barium chloride.

The results of three experiments were :—

| Experiment. | $(\mu - 1)10^6$. | | |
|-------------|-------------------|---------------|-------------------|
| | By weighing. | By titration. | By precipitation. |
| 1 | 707 | — | — |
| 2 | 736 | 739 | — |
| 3 | 737 | 748 | 727 |

We believe the method of weighing by difference to give the most accurate results, and we therefore adopt 737 as the most probable value for the index. But the difficulties of the experiment render this figure not altogether beyond doubt.

The refractivities of these sulphur compounds are very interesting, owing to the fact that they depart widely from the additive values.

The refractive index of gaseous sulphur (S_2), for $\lambda = 5893$, has been recently found by the authors to be 1.001111. That of oxygen (O_2) may be taken as 1.000270. Hence the refractivity of sulphur dioxide, by the additive rule, would be $555 + 270 = 825$, whereas experiment shows it to be 661, a decrease of nearly 20 per cent. Similarly, the refractivity of SO_3 , by the additive rule, is 960, but by experiment 737, a decrease of 23.2 per cent.

The interest of these curious figures is enhanced by similar results for other sulphur compounds. The refractivity of gaseous sulphuric acid has not yet been measured, but that of the liquid has been observed by

Baden-Powell, Gladstone, and Nasini. The figures of the latter,* which are the most recent, are as follows:—

| Compound. | Density, $\frac{23^{\circ}\text{C.}}{4^{\circ}\text{C.}}$ | Light. | Index. |
|--|---|--------|--------|
| $\text{H}_2\text{SO}_4 + \frac{1}{2}$ per cent. H_2O | 1.8273 | D | 1.4292 |

By means of Lorentz' formula,

$$\mu - 1_{\text{gaseous}} = \frac{\mu^2 - 1_{\text{liquid}}}{\mu^2 + 2_{\text{liquid}}} \cdot \frac{3}{2} \cdot \frac{\text{Molecular weight}}{\text{Liquid density}} \cdot \frac{0.00009}{2},$$

we can obtain a fair approximation to the gaseous index for the theoretical density, *i.e.*, that in which the number of molecules is the same as in unit volume of hydrogen at normal temperature and pressure.

Calculated thus, and with a correction for the water present, the index of gaseous H_2SO_4 is 1.000933. The additive value for the index is 1.001234. Hence the decrease on combination is $24\frac{1}{2}$ per cent.

With these may be compared the values of the refractive indices of the hexafluorides of sulphur, selenium, and tellurium, determined by us with Dr. E. B. R. Prideaux.†

| Compounds. | Refractivities. | | Difference of col. 3—col. 2. | Difference per cent. of col. 3. |
|----------------|-----------------|-----------------------------|------------------------------|---------------------------------|
| | Observed. | Additive value. | | |
| SF_6 | 783 | $6 \times 96 + 555 = 1131$ | 348 | —30.2 |
| SeF_6 | 895 | $6 \times 96 + 782 = 1358$ | 463 | —34.1 |
| TeF_6 | 991 | $6 \times 96 + 1247 = 1823$ | 832 | —45.2 |

We have pleasure in acknowledging assistance derived from a grant from the Royal Society, and have to thank Professor Trouton for placing at our disposal the resources of the Physical Laboratory of University College London.

* Nasini, 'Ber. d. Deut. Chem. Ges.,' vol. 15, p. 2885 (see Dufet, 'Données Numériques' vol. 1, p. 118).

† "Some Reactions and New Compounds of Fluorine," E. B. R. Prideaux, 'Chem. Soc. Trans.,' 1906, vol. 89, p. 330.

On the Dispersion of Gaseous Mercury, Sulphur, Phosphorus, and Helium.

By C. CUTHBERTSON, Fellow of University College, London, and E. PARR METCALFE, B.Sc., 1851 Exhibition Scholar.

(Communicated by Professor F. T. Trouton, F.R.S. Received February 11,—
Read February 20, 1908.)

In continuation of previous work* on the refractive indices of certain elements in the gaseous state, we have measured the dispersion of the elements named above within the limits of the visible spectrum.

Jamin's refractometer was used, and the arrangement of the instrument was that described in our previous paper. But, as different wave-lengths had to be employed for the determination of the dispersion, the method of illumination was improved. Light from a Nernst filament was focussed on the slit of one of Messrs. Hilger and Co.'s fixed-deviation spectroscopes, and, in the focal plane of the resulting spectrum, a slit was placed capable of motion in that plane. The adjustment was calibrated by comparing the wave-length of the light passing through the slit with the reading of the drum of the spectroscope. By rotating the drum, light of any required wave-length could be obtained, and, by narrowing the slits, the spectrum was of sufficient purity to admit of two hundred bands being counted to one-fifth of their breadth.

With this arrangement two methods of procedure were employed. At first a separate observation was made of the refractive index at each wave-length selected, while the substance was heated until it had completely evaporated. But this plan is open to the serious objection that any error due to unequal disposition of the two tubes, unequal heating, buckling of the supports, or drift due to the heating of the mirrors, is not eliminated; and, since the dispersion is in all cases a small fraction of the refraction, such errors are of importance.

In order to avoid these disturbing causes, a second method was worked out by one of us (E. P. M.) which, as far as we know, has not been previously used.

Both interferometer tubes being vacuous, the mirrors and compensator are so adjusted that each of the interfering beams passes through the same thickness of glass, of air, and of silica. When this is the case the interference pattern, viewed by white light, presents the appearance of a train

* 'Phil. Trans.,' A, vol. 207, pp. 135—148, 1907.

of fringes, black and white at the centre, but rapidly becoming coloured as their distance from the centre increases. The only truly achromatic point in the interference pattern is the centre of the bright fringe between the two darkest fringes: at this point the relative retardation is zero for all wave-lengths. It is not difficult to pick out by eye the two darkest fringes. The adjustment is effected by rotating one mirror, or the compensator, until the cross-wire or pointer of the observing telescope lies exactly midway between these two fringes. The white light is then replaced by the monochromatic illumination.

If now the wave-length is changed continuously by slowly rotating the spectroscope drum, the central bright fringe remains in the same position relatively to the cross-wire; the only effect of varying the wave-length is to change the spacing of the fringes. This preliminary adjustment having been made, the dispersion of the vapour is measured thus.

The spectroscope drum is set to some convenient wave-length, *e.g.*, that of the green mercury line, which is specially suitable, both on account of the luminosity of the spectrum in that region, and because a mercury vapour lamp provides a handy standard for testing the accuracy of the correspondence of the drum reading with the wave-length of the light passing through the slit. Then the weighed charge is slowly evaporated in one of the interferometer tubes. The fringes which cross the pointer are counted, and, when they have again come to rest, the spectroscope drum is rotated slowly. This will, in general, cause the fringes to move across the pointer. As each fringe reaches the pointer the corresponding wave-length is read off the drum. In this way we get, in one operation, the fringe readings for the particular quantity of vapour used, for thirty or forty points along the visible spectrum.

It must be remembered that the rate of variation of fringe reading with wave-length is not simply a function of the dispersion of the gas alone.

If N = number of fringes observed, λ = wave-length, n = refractive index of the gas, then $N = k \frac{(n - 1)}{\lambda}$, where k is dependent only on the dimensions of the apparatus, and

$$\frac{dn}{d\lambda} = \frac{1}{k} \left(N + \lambda \frac{dN}{d\lambda} \right).$$

Of the terms on the right-hand side, the first represents the effect of introducing the gas into the refractometer tube, the wave-length remaining the same; the second expresses the movement of the fringes when the wave-length is varied, while the gas pressure is constant.

The terms being of the same order of magnitude, they must be measured with the same degree of accuracy.

It is, of course, highly desirable that the achromatic point of zero retardation, when both interferometer tubes are vacuous, should not suffer displacement during the operation of measuring the fringes, through uneven temperature conditions or mechanical shocks. As soon as possible, therefore, after taking a set of readings, the vapour is rapidly condensed in its tube, and the coloured fringes of white light are examined.

In practice it is convenient to take several slow readings of the number of fringes for one wave-length, so as to obtain it correct to the nearest integer. Any outstanding fraction is best estimated by vaporising the charge as quickly as possible; for in this way the zero has but little time to "drift" before all the fringes have passed.

When refractometer tubes of fused silica* are used, difference of thickness of the end plates is almost unavoidable, owing to the necessity of refiguring and polishing them after they have been fused into the bore of the tubes. This difference introduces a slight complication. Suppose that an attempt is made to compensate for a slab of silica of thickness t_s and refractive index n_s placed in the path of one beam by putting in the other a slab of glass of thickness t_g and index n_g . Then the condition for achromatism becomes

$$t_s \frac{dn_s}{d\lambda} - t_g \frac{dn_g}{d\lambda} - (t_s - t_g) \frac{dn_A}{d\lambda} = 0,$$

where n_A = refractive index of air.

The dispersion of air is so small, compared with that of glass or of silica, that the last term may be neglected. So that, for the achromatisation to extend over any range of wave-length, it is necessary that the ratio of the dispersions of the two slabs shall be constant throughout that range. This condition is not satisfied in the case of silica and glass, so that perfect chromatic compensation is not possible. The difficulty could, of course, be met completely by using a compensator of the type used by Jamin, the plates being made of fused silica. But a simpler way was found to be quite satisfactory. The silica slab was compensated for as well as possible with glass; and, the tubes remaining vacuous, the spectrum was traversed. The position of the zero fringe was observed to shift by about one-tenth of a fringe width. This displacement was plotted against wave-length, and thus it was easy to correct for the effect in the dispersion curves of the gases and vapours dealt with.

* Cuthbertson and Metcalfe, *loc. cit.*

Mercury.

A single charge of mercury was sufficient to yield concordant results. Numerous series of readings were taken by the differential method. The curves plotted from them were found to agree well, and from 43 of the best observations we select the following values of the refraction at three points of the spectrum—

| λ . | $(\mu - 1) 10^6$. |
|-------------|--------------------|
| 6900 | 1840 |
| 5893 | 1866 |
| 4900 | 1920 |

The value obtained for sodium light agrees well with that obtained by C. Cuthbertson three years ago, and is identical with that found by E. P. Metcalfe last year.

Adopting these numbers, the refraction curve is expressed in the form given by Cauchy, as

$$\begin{aligned}\mu - 1 &= 0.001755 + \frac{3.96}{\lambda^2 10^{13}} \\ &= 0.001755 \left(1 + \frac{2.265}{\lambda^2 10^{10}} \right).\end{aligned}$$

The rate of change of index is about four times that of air, for which the corresponding formula is, according to Scheel,

$$\mu - 1 = 0.00028705 \left(1 + \frac{5.65}{\lambda^2 10^{11}} \right).$$

Sulphur.

Two charges of sulphur were used. In the spectrum of this element there is an absorption band extending from the violet almost to the red, and, with the first charge, readings could not be obtained beyond the yellow. At $\lambda = 5183$, light failed after 108 bands had passed, and at $\lambda = 5050$ only 75 bands could be read.

In order to obtain values beyond this point, the weight of sulphur had to be diminished to 0.00664 gramme, giving about 31 bands at $\lambda = 5893$, the lowest number from which fair accuracy could be obtained. From 35 observations we deduce the following as the best values for the refractivity of sulphur at three points in the spectrum—

| $\lambda \cdot 10^{-8}$ cm. | $(\mu - 1) 10^6$. |
|-----------------------------|--------------------|
| 6562.8 | 1096.5 |
| 5893 | 1111 |
| 5183.8 | 1128 |

Using these values, the curve of refraction can be expressed by—

$$\begin{aligned}\mu - 1 &= 0.0010457 + \frac{2.222}{\lambda^2 10^{13}} \\ &= 0.0010457 \left(1 + \frac{2.1249}{\lambda^2 10^{10}} \right).\end{aligned}$$

The two independent values obtained for the refraction at $\lambda = 5893$ (1105 and 1111) agree well with that found by C. Cuthbertson in 1905 (1101) with glass tubes and a lower temperature.

If we attempt to determine the position of the centre of the absorption band from the formula $\mu - 1 = \frac{a}{p^2 - \omega^2}$, we find from the first and second observations $\lambda_0 = 1492$, and from the first and third $\lambda_0 = 1378$; values which are not very concordant.

We have previously observed that,* until values of the refractivities for infinite wave-lengths could be obtained, it was useless to examine more closely the curiously simple ratios between the refractivities of allied elements which were found to obtain at the D lines. It was shown that, at that point of the spectrum, the ratio of the refractivities of P to N, S to O, Cl to F, and Ar to Ne, was very nearly four. It is interesting, therefore, to compare the value now found for sulphur with the refractivity of oxygen for infinite wave-lengths.

The dispersion of oxygen does not appear to have been fully investigated, but Natanson† has calculated the value of the refractivity for λ_∞ from Mascart's figures to be 266.3, and Koch‡ has found for $\lambda = 86.9$ the number 266.1.

Adopting the mean of these determinations, the ratio of the refractivities of sulphur to oxygen for infinite wave-lengths is, therefore, $10457/2662 = 3.928$, which only differs from the number 4 by 1.8 per cent.

If it be remembered that the presence of the absorption band in the violet, and possibly of one of the red, must disturb the values from which the refraction curve is calculated, the coincidence is good. It is closer than that between the indices of the two elements at the D lines.

It is interesting also to compare the dispersions of the two elements. The refraction curve of oxygen, calculated from Mascart's figures, is

$$\mu - 1 = 0.002663 \left(1 + \frac{5.07}{\lambda^2 10^{11}} \right).$$

* 'Phil. Trans.,' A, vol. 207, p. 146, 1907.

† "On the electro-magnetic theory of dispersion and extinction," 'Bull. de l'Acad. des Sciences de Cracovie,' Ap., 1907, p. 336.

‡ 'An. d. Physik,' vol. 17, p. 665, 1905.

Thus the rate of change of refraction of sulphur is about four times that of oxygen.

One of our observations in the extreme red ($\lambda = 6870$) was abnormally low, which would suggest the presence of an absorption band in the infra red. So far as we know, the spectrum of sulphur vapour has not been investigated in this region.

Phosphorus.

In this case also a single charge of the element was used.

From thirty-nine observations we deduce the following most trustworthy values :—

| λ . | $(\mu-1) 10^6$. |
|-------------|------------------|
| 6800 | 1200 |
| 5893 | 1212 |
| 5100 | 1230 |

From these figures the refraction curve is :—

$$\begin{aligned}\mu-1 &= 0.001162 + \frac{1.777}{\lambda^2 10^{13}} \\ &= 0.001162 \left(1 + \frac{1.53}{\lambda^2 10^{10}} \right).\end{aligned}$$

The value now found for $\lambda = 5893$ agrees well with C. Cuthbertson's earlier value (1197), but, like that of sulphur, the new value is about 1 per cent. higher than the old.

As in the case of sulphur and oxygen, it is interesting to compare the refractive index for infinite wave-lengths with that of nitrogen.

Scheel's values for the dispersion of nitrogen are expressed by the formula

$$\mu-1 = 0.00029061 \left(1 + \frac{7.70}{\lambda^2 10^{11}} \right).$$

Multiplying the refractivity for infinite wave-lengths by four we obtain 1162, which is identical with that found for phosphorus. Comparing the dispersions we find that the rate of change of refraction for phosphorus is almost exactly double that of nitrogen, while that of sulphur was about four times that of oxygen.

Helium.

The specimen of helium used in the experiment was kindly lent us by Sir W. Ramsay, to whom our thanks are due. It was obtained from thorianite and purified by Dewar's process of passing the gas through charcoal cooled with liquid air. The measurement of the dispersion of this element presents considerable difficulties owing to its smallness. With a tube nearly two metres long, and a difference of pressure of 760 mm.,

only about a hundred bands can be obtained in the yellow. The dispersion is less than $\frac{1}{2}$ per cent. of the refraction in the visible spectrum, so that the whole measurable effect between the red and violet is about one-third of a band, and, as it is almost impossible to read to less than one-tenth of a band, accurate results were not obtained. The principal difficulties were found in the change of zero of the refractometer with temperature, instability of the building, parallax in making readings in either the red or violet, and the determination of the wave-length employed.

In order to avoid this last source of error a further modification of the differential method was adopted. Enough helium was admitted to one tube to cause about a hundred bands to cross the field. Into the other tube air was then introduced until an exactly equal number of bands had passed in the opposite direction. The wave-lengths of the light employed were then changed from red to violet. In these circumstances any change in the position of the band which is on the pointer is due to the difference between the dispersions of air and helium. For the dispersion of air the formula of Kayser and Runge was assumed—

$$\mu = 1.00028787 + \frac{1.316}{\lambda^2} + \frac{3.600}{\lambda^4}.$$

The helium was repeatedly repurified, as it was found that it became contaminated by small bubbles of air creeping in during the manipulations.

Out of a large number of experiments we select six as the most trustworthy for the refraction at the D line.

These are as follows—

| 1907. | Oct. 1. | Oct. 14. | Oct. 21. | Oct. 23. | Nov. 13. | Dec. 18. |
|---------------|---------|----------|----------|----------|----------|----------|
| $(\mu-1)10^6$ | 34.871 | 34.859 | 34.836 | 35.022 | 35.008 | 34.946 |

The mean of these is 34.93, and this we adopt as the refractivity at $\lambda = 5893$.

For the dispersion the last and best series of experiments gave for the difference of refraction between $\lambda = 6500$ and $\lambda = 5300$ the following values—

$$\begin{aligned}
 (\mu-1)_{\lambda=5300} - (\mu-1)_{\lambda=6500} \\
 0.00000096 \\
 0.00000120 \\
 0.00000109 \\
 0.00000084 \\
 0.00000078 \\
 0.00000109
 \end{aligned}$$

The mean of these is 0.000000099, and, adopting this value, we obtain for the curve of refraction

$$\mu - 1 = 0.0000347 + \frac{8.3}{\lambda^{10.11}} = 0.0000347 \left(1 + \frac{2.4}{\lambda^{2.1011}} \right).$$

The difference between the values given above seems large; but it must be remembered that they represent direct determinations of the dispersion, which is, between the limits chosen, 1/350 part of the refractivity. They correspond, therefore, to an accuracy in the determination of the refractivity of any particular ray 350 times as great.

We think the refractivity can be trusted to $\frac{1}{4}$ per cent., but the dispersion to not less than 10 per cent.

Thus, the dispersion of helium bears to the refraction a ratio of one-half to one-third that which the dispersion of air bears to its refraction.

The figures given are those for a monatomic gas. For comparison with the other elements they should be doubled.

In 1901 Sir William Ramsay and Dr. Travers found for helium, with white light, the value 1.0000363. Our value is 3.75 per cent. less. If this difference were due to greater purity of the gas there should be a corresponding decrease in the density. But an experiment on the specimen we used gave a density of 1.994 against 1.98 adopted by Ramsay and Travers, so that the discrepancy cannot be explained in this way, and may be attributed to our good fortune in having a larger quantity of the gas than its discoverers could command.

In a previous paper, by C. Cuthbertson,* attention was drawn to the simplicity of the ratios between the refractivities of the five inert gases. The following table shows that, with the new value for helium now obtained, the coincidence is even better:—

| Element. | Refractivities. | | Ratios. | Divergence per cent. | |
|---------------|---------------------|--------------------|---------------|----------------------|------------------|
| | Ramsay and Travers. | C. C. and E. P. M. | | Argon standard. | Helium standard. |
| Helium | 36.3 | 34.93 | $\frac{1}{4}$ | +2.3 | 0.0 |
| Neon | 68.7 | — | $\frac{1}{2}$ | -3.2 | -1.7 |
| Argon | 284.0 | — | 2 | 0.0 | +1.6 |
| Krypton | 425.0 | — | 3 | -0.2 | +1.4 |
| Xenon | 689.0 | — | 5 | -3.0 | -1.4 |

There is still room for improvement which may be found when the indices of the other gases are remeasured after being purified by absorption over cold charcoal.

* 'Phil. Trans.,' A, vol. 204, p. 323, 1905.

The results now obtained may be summarised as follows:—

$$\text{Mercury} \dots\dots\dots \mu-1 = 0\cdot001755 \left(1 + \frac{2\cdot265}{\lambda^2 10^{10}}\right).$$

$$\text{Sulphur} \dots\dots\dots \mu-1 = 0\cdot001046 \left(1 + \frac{2\cdot125}{\lambda^2 10^{10}}\right).$$

$$\text{Phosphorus} \dots\dots\dots \mu-1 = 0\cdot001162 \left(1 + \frac{1\cdot53}{\lambda^2 10^{10}}\right).$$

$$\text{Helium} \dots\dots\dots \mu-1 = 0\cdot0000347 \left(1 + \frac{2\cdot4}{\lambda^2 10^{11}}\right).$$

The dispersion of mercury is about four times that of air.

The index of sulphur for infinite waves is, within 2 per cent., four times that of oxygen. Its dispersion is, not so exactly, four times that of oxygen.

The index of phosphorus, for infinite waves, is exactly four times that of nitrogen. Its dispersion is almost exactly twice that of nitrogen.

The index of helium is, within 1·6 per cent., one-eighth of the best existing value for the index of argon. Its dispersion is about three-sevenths that of air.

We have great pleasure in expressing our cordial thanks to Professor Trouton and the staff of the Physical Laboratory at University College, London, for assistance and advice, and to the Royal Society for a grant in aid of the research.

On the Electrical Resistance of Moving Matter.

By Professor F. T. TROUTON, F.R.S., and A. O. RANKINE, B.Sc., University College, London.

(Received February 20,—Read March 5, 1908.)

The question of relative motion between the earth and the neighbouring ether has been under discussion for many years. It has, from time to time, been the subject of important investigations; but these have all resulted negatively. The experiment about to be described is not different from them

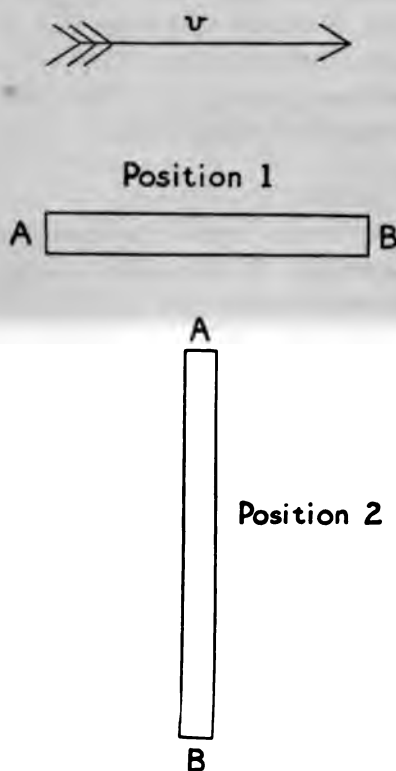


FIG. 1.

sectional area a moving through the ether in a direction parallel to its length with a velocity v . Let ρ be its specific resistance and R its total electrical resistance. The relation

$$R = \rho \frac{l}{a} \quad (1)$$

in this respect, yielding, as it does, no definite information on the main point. It was suggested and commenced by one of us some years ago; but the serious difficulties which invariably attend measurements of such delicacy have delayed its completion till the present time. Indirectly, the aim was to measure the direction and magnitude of ether-drift; the actual method having been to attempt to demonstrate the existence of the Fitzgerald-Lorentz shrinkage which has been supposed to mask the effect in the direct experiments of Michelson and Morley, and of Trouton and Noble. It may be as well to say at once that if such a shrinkage be real, it is in this experiment also obscured by some other exactly compensating change or changes, no effect approaching that to be otherwise expected having been observed.

The principle of the measurement is a very simple one. Imagine a uniform wire AB (fig. 1) of length l and cross-

is then true. Differentiating logarithmically, we obtain

$$\frac{\delta R}{R} = \frac{\delta \rho}{\rho} + \frac{\delta l}{l} - \frac{\delta a}{a}. \quad (2)$$

Now suppose that the wire AB is turned through a right angle, so that its length is perpendicular to the velocity v . According to the Fitzgerald-Lorentz shrinkage hypothesis, the length of the wire will be thus increased by a small amount δl , such that $\frac{\delta l}{l} = \frac{1}{2} \left(\frac{v}{V} \right)^2$, where V is the velocity of light, and all powers of v/V higher than the second have been neglected, v being supposed very small compared with V . Writing β for v/V , we have

$$\frac{\delta l}{l} = \frac{1}{2} \beta^2.$$

This is not the only change in dimensions to be expected. In the first position of AB both dimensions of the cross section are perpendicular to the direction of motion, while in the second position one remains perpendicular, but the other becomes parallel. A decrease in this latter dimension of the relative amount $\frac{1}{2} \beta^2$ will cause a diminution of a in the same ratio. Therefore

$$\frac{\delta a}{a} = -\frac{1}{2} \beta^2.$$

Substituting in (2), it follows that

$$\frac{\delta R}{R} = \frac{\delta \rho}{\rho} + \beta^2.$$

If it be supposed that the specific resistance of the material forming the wire is independent of the direction of motion, $\delta \rho / \rho = 0$, and therefore $\delta R / R = \beta^2$. Hence, on the above assumptions, it is to be expected that the resistance of a wire with its length perpendicular to the ether-drift will be greater than when parallel in the ratio $(1 + \beta^2) : 1$. On the other hand, should there be no change in total resistance, two alternatives present themselves. Either there is no alteration of length of the kind supposed, or the specific resistance changes in such a way as to compensate it. In the latter case the law of change would be that the specific resistance of a material to a current flowing parallel to the ether-drift is greater than that at right angles to this direction in the ratio $(1 + \beta^2) : 1$. The present investigation was, however, based upon the assumption that the specific resistance was constant; and the object in view was to detect a variation of the resistance of a wire with direction.

The method used was the ordinary Wheatstone bridge method of comparing resistances, specially adapted, of course, to the particular requirements of this case. With certain modifications, to be described later, the arrangement was as follows:—Four coils of wire, each wound upon a flat rectangular frame,

formed the four arms of a Wheatstone bridge. By suitably adjusting the position of any frame, the wire on it, with the exception of the small part used in turning the corners, could be made to take up any desired direction. The frames were arranged horizontally on a stand so that the wires forming opposite arms of the bridge were parallel, and those forming adjacent arms perpendicular to one another. The arrangement is shown diagrammatically in fig. 2. The lines marked 1, 2, 3, and 4, must be taken as representing the direction of the major part of the wire on the corresponding coil. If the resistances of 1, 2, 3, and 4 are equal, there will be no current through the galvanometer. Suppose that the coils 1 and 3 are parallel, and the coils 2 and 4 perpendicular to the ether-drift; also that balance is obtained, and the resistance of each coil is equal to R . If, now, the stand be rotated through

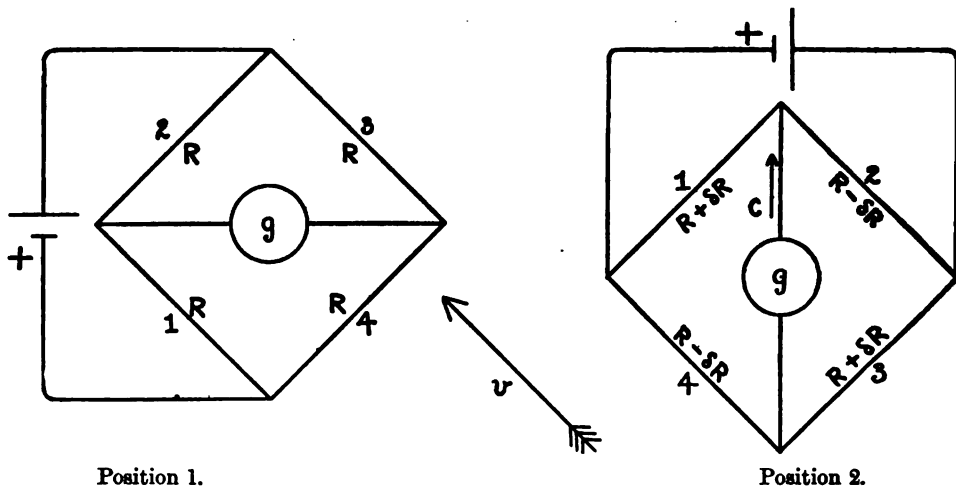


FIG. 2.

a right angle, so that 1 and 3 become perpendicular, and 2 and 4 parallel to the drift, it is to be expected, on the previous assumptions, that 1 and 3 will each increase in resistance by an amount δR , and that 2 and 4 will each diminish by an equal amount. This would result in the balance being destroyed; and a current of magnitude $E\delta R/R(R+g)$ would flow through the galvanometer in the direction indicated by the arrow. Here E represents the E.M.F. of the battery, and g the galvanometer resistance; and the internal resistance of the battery has been neglected. Or, if for some reason it has been impossible to obtain perfect balance in the first instance, and a small current flows in the galvanometer all the time, the change to be expected upon rotation in the magnitude of this current is measured also by $E\delta R/R(R+g)$. In other words, and remembering that the expected value of

δR is $R\beta^2$, a variation of current of value $\frac{E}{R+g} \cdot \beta^2$ is to be looked for. Since this expression contains so small a factor as $\beta^2 = (u/V)^2$, it is obvious that the measurement will be a difficult one; and this was indeed found to be the case, many effects, usually negligible in resistance measurements, now being comparatively large. Their elimination—or rather, partial elimination, for they were to the last not entirely absent—was very tedious, and at times appeared almost hopeless; but it was at last effected in the manner about to be described.

The first difficulty was due to the presence of thermoelectric currents, which, at first, varied so rapidly as to make determinations impossible. It was very soon found that junctions, even between pieces of the same wire, which were originally in the resistance arms, and the key in the galvanometer arm produced disturbances of such a serious character that they had to be omitted. Again, it was at first intended to effect balance by the movements of a slider on a thick copper rod, the other end of the galvanometer arm being permanently attached to the junction between the opposite arms. It was also hoped to be able to re-balance after rotation by a further movement of this slider; this method, however, had to be abandoned, owing to the impossibility of moving the slider without producing further heating. Another objection to the use of this thick copper rod lay in the fact that it was the cause of a difference of temperature between the two ends of the galvanometer arm. Practically the same current flowed in this rod and in the thin wires of which the coils were made, and to which the other end of the galvanometer wire was attached. Owing, therefore, to the heating effect of the current itself, a permanent difference of temperature became established at the two terminals referred to. To effect the removal of these disturbances, the following means were adopted. The four bridge arms were made of two unbroken pieces of uniform wire soldered together at the points at which the current was led in from the battery. Here, of course, small variations in potential were ineffective, producing, in the case of perfect balance, no current through the galvanometer, and, even when a small current was flowing, causing changes of the second order only in it. There were no junctions at all in the wires whose resistances were being compared. The galvanometer was inserted by means of a slider (as indicated in fig. 3), which joined through the former the mid points of the two unbroken wires previously referred to. Contact was made by simple pressure between crossed wires. It was, of course, impossible to avoid using two junctions here; but, by arranging them very close together, and because they were now equally heated by the current, the thermoelectric effects were reduced practically to zero.

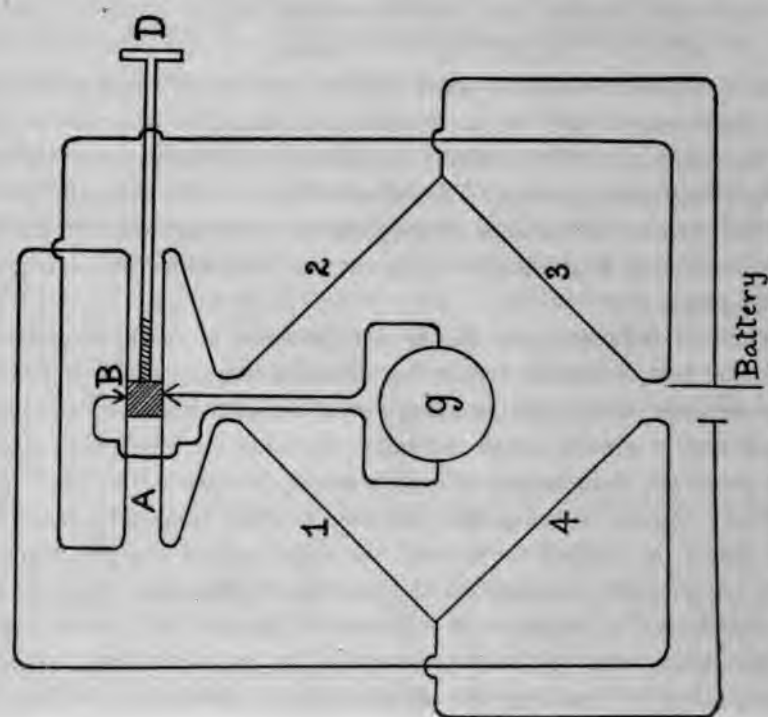
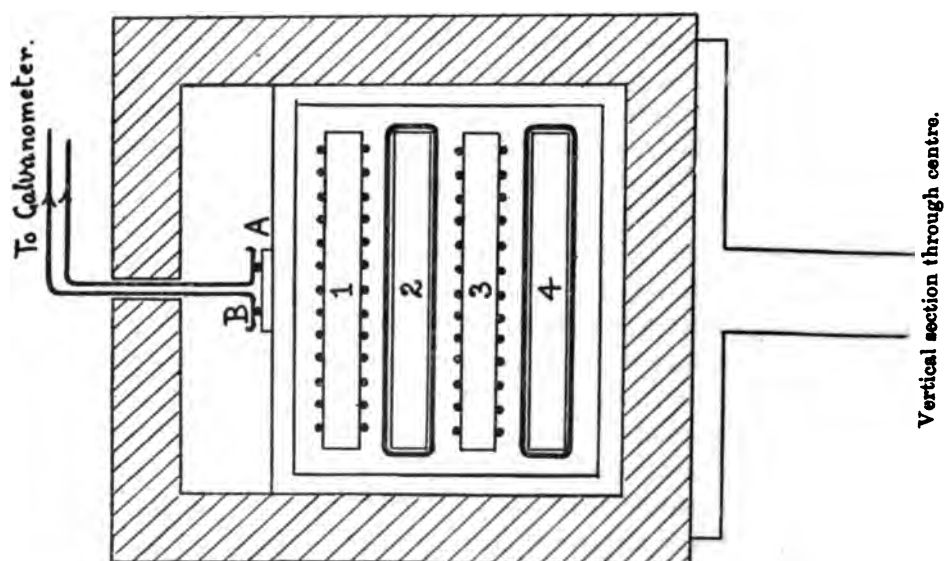


Diagram of arrangement of apparatus.



Another and more persistent disturbance arose from unequal heating producing changes of resistance in the coils. It soon became evident that it would be impossible to use uncovered wire; but even when the wire used (originally copper) was thickly covered with gutta-percha, the effect of heating was too large to make definite measurements. The coils were arranged one above the other on a stand, and were turned about a vertical axis inside an enclosure made of wood and felt. The temperature of the air varied from point to point of this enclosure; and, upon rotation of the stand, changes of resistance occurred, owing to the coils occupying different positions in it. Moreover, even when the coils were not rotated, the behaviour of the current in the galvanometer indicated a gradual increase of resistance in the upper coils relative to the lower ones. This was, doubtless, due to the warming of the air in the enclosure by the currents which were flowing; and, the warm air rising, the upper resistances increased more rapidly than those lower down. With the exception of this latter effect, the disturbances were removed by rotating the enclosure itself with the stand, thus carrying the temperature distribution of the air round, and by making the coils with manganin wire instead of copper, on account of the much smaller temperature coefficient of the former. The relative increase of resistance of the upper coils was thus made much more gradual, but it has been found impossible to entirely eliminate the effect, and it has been necessary, even in the final form of the apparatus, to take time readings of the current for the various positions of the stand. The variation of the current in the galvanometer, due to this cause, is now, however, sufficiently slow to make it quite easy to distinguish from it the immediate genuine effect which is looked for.

A further spurious effect was that due to alterations in resistance which were brought about by stresses introduced in rotating the stand. As it happened, the magnitude of this effect was just of the order of that expected; and this at one time led us to suspect a positive result. The apparatus at that time was not in its final form, and was not adapted for rotations other than a right angle; so it was impossible to make an absolutely conclusive test. The balancing bridge (shown in fig. 3) was not then rotated with the rest of the apparatus, and thus there arose a possibility of strain in the wires forming parts of the resistances which were being compared. This difficulty was finally surmounted by rotating the whole of the apparatus bodily, with the exceptions of the galvanometer and battery. This removed the strain to the wires leading to the two latter, *i.e.*, to places where small changes of resistance were unimportant.

Finally, it was necessary to remove an effect which can hardly be called a disturbance. As has been already pointed out, the use of a key was

dispensed with in the galvanometer arm. The result of permanent contact was to produce an induction current in the galvanometer when the apparatus was turned round. This would not have mattered if it had not been necessary to take time readings on account of heating effects. Readings were eventually taken every quarter minute, and the galvanometer was not sufficiently damped to make this possible when the throws were large. In the whole region of space occupied by the stand, the magnetic field of the earth was reduced practically to zero by suitably disposing 16 permanent magnets in the neighbourhood. The temporary induction effect upon rotation died out then completely in about five or six seconds after that rotation.

The final arrangement of the apparatus is shown diagrammatically in fig. 3. The four coils, 1, 2, 3, and 4, are arranged on a stand as before indicated, and above them (and also fixed to the stand) the balancing bridge A. This latter merely consists of about 5 or 6 cm. of bared wire drawn taut on a wooden stand. The wires are here parallel and about a centimetre apart, and the slider B, through which wires lead to the galvanometer, is movable along their length by means of a screw D. The slider B consists of an arrangement by which the two wires from the galvanometer are pressed down by springs, one on each wire of the balancing bridge, and balance is obtained by using the screw D. The whole of the apparatus, with the exception of the galvanometer and battery, is encased in a cubical double-walled enclosure, which is fixed to a horizontal turntable, the interspace between the two walls of the enclosure being filled with cork dust for purposes of thermal insulation. The screw-head D projects outside the enclosure, so that adjustments may be made without opening the latter, and the wires to the battery and galvanometer are led out through a small hole at the top on the vertical axis of rotation.

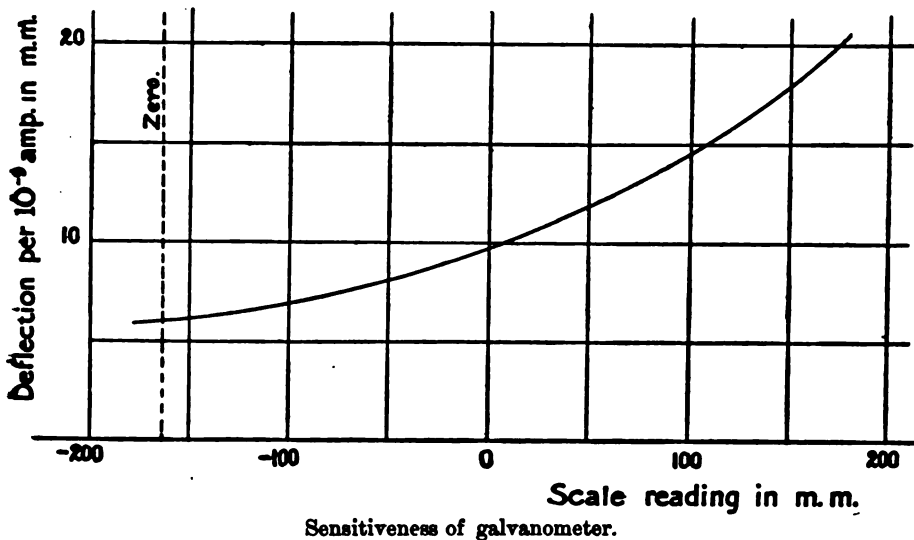
The battery used is a single-storage cell. The galvanometer is of the Du Bois type—a low-resistance suspended needle galvanometer, trebly shielded with soft iron. These shields are very effective in removing magnetic disturbances such as those caused by the neighbouring electric railway, and they are found to be very necessary in delicate work of this description. The behaviour of the needle is examined by using a Nernst lamp and scale at about $2\frac{1}{2}$ metres distant, and, in its most sensitive state, a scale deflection of about 4 cm. can be obtained with a current of 10^{-9} ampere.

In the actual experimental work the field about the needle was found to be variable, and the sensitiveness increased with the scale reading. This is shown in fig. 4, where the deflections produced by an additional 10^{-9} ampere are plotted against the scale reading. The expected deflection upon rotation,

therefore, varied with the scale reading at that time, and use was made of this calibration in calculating the results.

With regard to the dimensions of the apparatus, the coils were made of gutta-percha-covered 24 manganin wire, each of them consisting of 16 turns round a 6-inch square flat frame. Almost exactly $1/7$ part of the wire was not horizontal, *i.e.*, the parts used in turning corners, and in leading to the bridge. This fraction was, therefore, not expected to contribute to the calculated change of resistance. The resistance of each coil was 11.16 ohms and that of the galvanometer 10 ohms. The E.M.F. of the storage cell was slightly variable, but was taken as having an average value of 2.1 volts, and its internal resistance has been regarded as negligible.

FIG. 4.



To calculate the expected variation in current upon rotation, therefore, we substitute the above values in the formula

$$\delta C = \frac{E}{R+g} \beta^2.$$

This must, however, be reduced by $1/7$ part, in order to allow for the non-contributing parts of the wire. We have

$$\begin{aligned} \delta C &= \frac{6 \times 2.1}{7 \times 21.16} \cdot \beta^2 \text{ ampere} \\ &= \frac{6}{7} \cdot \frac{\beta^2}{10} \text{ ampere, approximately.} \end{aligned}$$

If the earth's orbital motion only be taken into account, the value of β^2 is

approximately 10^{-8} , and in this case the expected change in current would be

$$0.86 \times 10^{-9} \text{ ampere.}$$

Such a current would produce, in the neighbourhood of the scale reading O (fig. 4), a deflection of 8.4 mm., but the particular deflection to be expected depends on the part of the scale at which the determination is made.

Moreover, if the sun's proper motion be allowed for, the value of β^2 is dependent upon the time of year, and a special calculation is required in each case. This has been done for the results given later in Tables II and IV. The values of β^2 , the time of horizontal drift, and its azimuth when horizontal, were obtained from the values given in the paper describing the ether-drift experiments of Trouton and Noble.*

The method of taking observations was as follows:—A time was chosen when the calculated direction of the total drift was horizontal. By means of moving the slider B (fig. 3), an attempt was made to reduce the current in the galvanometer to zero. This, however, was very difficult, and not essential. Usually, the spot of light, whose position indicated the magnitude of the galvanometer current, was merely brought somewhere within the limits of the scale, and possibly there would be already a current of about 10^{-8} ampere. The spot of light would be found to slowly creep in the direction indicating a relative increase of resistance in the upper coils. Its velocity would, however, become much smaller after the current had been flowing for some time. (It may here be pointed out that, as a rule, the battery was, on this account, connected up with the bridge some hours before taking an observation.) The turntable was then rotated until one pair of coils became parallel to the drift, and a reading was taken at a particular instant. The turntable was then turned at once through a right angle, and a further reading taken after 15 seconds. Immediately the turntable was restored to its original position, another reading following after 15 seconds, and so on for about 20 reversals. Thus a set of 20 readings, at half-minute intervals, was obtained for each of the two positions of the stand.

Unfortunately, owing to mechanical shaking of the galvanometer (a disturbance which is never absent in London except in the early hours of the morning), it was impossible in the daytime to take readings nearer than 1 mm., although the optical definition was otherwise sufficiently good to admit of estimation to $1/10$ mm.

The following set of observations is typical:—

* 'Phil. Trans.,' A, vol. 202, pp. 165—181.

Table I.

Date, December 16, 1907. Time, 4.40—4.50 P.M. Azimuth of horizontal drift, measured eastwards from meridian, $\frac{1}{2}\pi + 42^\circ$.

Readings on scale (measuring the values of galvanometer current):—

| Azimuth of 1 and 3 (parallel drift) —48°. | Azimuth of 1 and 3 (perpendicular drift) +42°. | Azimuth of 1 and 3 (parallel drift) —48°. | Azimuth of 1 and 3 (perpendicular drift) +42°. |
|---|--|---|--|
| mm. —14 | mm. —15 | mm. —39 | mm. —41 |
| —17 | —18 | —42 | —43 |
| —20 | —20 | —45 | —45 |
| —22 | —25 | —47 | —47 |
| —25 | —26 | —49 | —51 |
| —28 | —29 | —52 | —53 |
| —30 | —31 | —53 | —54 |
| —32 | —32 | —54 | —56 |
| —33 | —36 | —56 | —57 |
| —36 | —38 | —57 | —58 |
| —38 | —39 | —60 | —63 |
| | | —65 | |

It will at once be apparent that there is no general tendency for the numbers in one column to be in excess of those in the other by the expected amount, viz., 10.9 mm. It is somewhat difficult, however, to determine the best method of interpreting them, for the purpose of discovering the limits of measurement of the apparatus. The form of the general time variation in current (so called to distinguish its immediate effects attributable to rotation) is unknown and not necessarily linear; hence, to take the difference of the means of the numbers in the two columns is only approximate. This latter was the method at first adopted, but although the results were satisfactory enough where the general current variation was practically linear, in cases where this condition did not exist discordant values of the difference were obtained, according to the number of observations utilised. Eventually the method about to be described was adopted as giving the most consistent results.

The following is an ideal set of readings, $a_1, a_2 \dots a_n$ being those for one position of the coils, and $b_1, b_2 \dots b_{n-1}$ those for the other position:—

| Differences. | Readings. | | Differences. |
|--|-----------|-----------|--|
| | a_1 | b_1 | $\frac{1}{2}(a_1 + a_2) - b_1$ |
| $a_2 - \frac{1}{2}(b_1 + b_2) \dots\dots\dots$ | a_2 | b_2 | $\frac{1}{2}(a_2 + a_3) - b_2$ |
| $a_3 - \frac{1}{2}(b_2 + b_3) \dots\dots\dots$ | a_3 | b_3 | \vdots |
| | \vdots | \vdots | \vdots |
| $a_{n-1} - \frac{1}{2}(b_{n-2} + b_{n-1}) \dots$ | a_{n-1} | b_{n-1} | $\frac{1}{2}(a_{n-1} + a_n) - b_{n-1}$ |
| | a_n | | |

$$\frac{(a_2 + a_3 + \dots + a_{n-1}) - \frac{1}{2}(b_1 + b_{n-1}) - (b_2 + b_3 + \dots + b_{n-2})}{n-2}$$

= Mean of differences in first column.

$$\frac{\frac{1}{2}(a_1 + a_n) + (a_2 + a_3 + \dots + a_{n-1}) - (b_1 + b_2 + \dots + b_{n-1})}{n-1}$$

= Mean of differences in last column.

The expression in the first column represents the difference between a particular value of a and the mean of the values of b , just before and just after, while that in the third column represents the difference between the mean of two successive values of a and the intermediate value of b . The means of the differences on the two sides respectively are given below, and they are to be expected to be equal to one another. This turns out to be very nearly true, and the final mean of these two numbers has been recorded in Tables II, etc., as measuring the observed excess of the " a " column over the " b " column.

For instance, take the numbers given in Table I. Here $n = 23$.

$$\text{Mean of differences in first column} = \frac{-835 + 39 + 799}{21} = \frac{3}{21} = +0.14 \text{ mm.}$$

$$\text{Mean of differences in last column} = \frac{-39.5 - 835 + 877}{22} = \frac{2.5}{22} = +0.11 \text{ mm.}$$

The final mean is therefore $+0.13$ mm., and this measured the change in current caused by the rotation of the coils in this particular case.

Now, by reference to the magnitude of the ether-drift on this particular day, and to the curve of sensitiveness of the galvanometer (fig. 4), it will be seen that the expected difference of scale reading is $+10.9$ mm. This certainly does not exist; and, in view of the fact that readings were made correct to 1 mm. only, there is reason for supposing that the observed difference is due to error in observation.

The following tables are records of the other observations taken:—

Table II.

These observations were made at the best times according to the calculations of Trouton and Noble, *i.e.*, when the resultant drift is horizontal.

| Date. | Time. | Magnitude of drift. | 1st azimuth of 1 and 3. | 2nd azimuth of 1 and 3. | Calculated difference of reading. | Observed. |
|-------------|-------|---------------------|-------------------------|-------------------------|-----------------------------------|-----------|
| Dec., 1907. | P.M. | miles/sec. | ° | ° | mm. | mm. |
| 11 | 4.50 | 22.1 | -44 | +46 | + 7.5 | 0.0 |
| 12 | 5.0 | 22.8 | -44 | +46 | +11.5 | +0.2 |
| 13 | 4.45 | 22.4 | -45 | +45 | + 7.7 | +0.1 |
| 16 | 4.40 | 22.9 | -48 | +42 | +10.9 | +0.1 |
| 19 | 4.25 | 23.8 | +40 | -50 | -11.8 | +0.2 |
| Jan., 1908. | | | | | | |
| 8 | 3.0 | 25.7 | -63 | +27 | +11.4 | -0.2 |

Table III.

In the following cases rotation was through 180° , so that no effect is to be expected.

| Date. | Time. | 1st azimuth of 1 and 3. | 2nd azimuth of 1 and 3. | Observed difference. |
|-------------|-------|-------------------------|-------------------------|----------------------|
| Dec., 1907. | P.M. | ° | ° | mm. |
| 13 | 4.45 | -45 | $(\pi/2) + 45$ | -0.2 |
| 16 | 12.5 | + 2 | $\pi + 2$ | +0.3 |
| 16 | 4.25 | -48 | $(\pi/2) + 42$ | 0.0 |
| 19 | 12.25 | 0 | $-\pi$ | -0.2 |
| Jan., 1908. | | | | |
| 8 | 3.45 | -63 | $(\pi/2) + 27$ | -0.1 |

Table IV.

The following three observations are tests for the earth's orbital motion alone, no attention being paid to the effect of the sun's proper motion.

| Date. | Time. | 1st azimuth of 1 and 3. | 2nd azimuth of 1 and 3. | Calculated difference. | Observed. |
|-------------|-------|-------------------------|-------------------------|------------------------|-----------|
| Dec., 1907. | P.M. | ° | ° | mm. | mm. |
| 16 | 12.15 | 2 | $(\pi/2) + 2$ | -5.5 | +0.2 |
| 19 | 12.5 | 0 | $(\pi/2)$ | -6.0 | +0.3 |
| 19 | 12.15 | 0 | -90 | -5.7 | +0.3 |

It will be noticed that the observed difference is sometimes of the same sign as that calculated, and at other times of opposite sign. We are, therefore, inclined to attribute it, as before suggested, merely to error of observation; however, even supposing it to be a real effect, its maximum value is less than 2 per cent. of that looked for.

It may be objected that the above method of experimenting is not the correct one—that, to be quite conclusive, no assumption as to the direction of the ether-drift should be made. With a view to settling this point and, incidentally, making use of the increased accuracy of reading possible at night time, the following sets of observations were made throughout the early morning hours of January 18 last. The freedom from vibration made estimation to 1/10 mm. as easy as 1 mm. readings in the daytime. The observations were spread over the whole time from 12 midnight to 4.15 A.M., and were, in a sense, a search for ether-drift. The results are calculated in the way previously indicated, and tabulated in five sections, each section containing the results of exactly similar treatment as regards rotation. Thus, Section I contains the three cases in which the first azimuth of 1 and 3 was 0° and the second azimuth 90° .

Table V.

| | Time. | 1st azimuth of 1 and 3. | 2nd azimuth of 1 and 3. | Observed difference of scale reading. |
|----------------|-------|----------------------------|----------------------------|--|
| | A.M. | $^\circ$ | $^\circ$ | mm. |
| Section 1..... | 12.0 | 0 | +90 | +0.18 |
| | 2.0 | 0 | +90 | +0.41 |
| | 4.0 | 0 | +90 | +0.32 |
| Section 2..... | 1.0 | 0 | -90 | -0.04 |
| | 3.0 | 0 | -90 | -0.04 |
| Section 3..... | 12.15 | -45 | +45 | +0.04 |
| | 2.15 | -45 | +45 | +0.05 |
| | 4.15 | -45 | +45 | -0.05 |
| Section 4..... | 1.15 | +45 | -45 | -0.04 |
| | 3.15 | +45 | -45 | -0.31 |
| Section 5..... | 12.35 | -90 | +90 | +0.14 |

In interpreting the results above recorded, careful attention should be paid to the treatment of the coils in any particular case. Since the readings are now made to 1/10 mm., we think that a difference which affects the first place of decimals measures a real effect produced by rotation. Thus, in the first section, the differences are of this magnitude and of the same sign. That they are not, however, due to an effect of ether-drift is proved by the

observations taken at intermediate times and recorded in Section 2. Here the coils were rotated in the opposite direction through 90° also, and no real effect was produced. It is obvious that, for measuring a genuine ether-drift effect, the direction of rotation through 90° is indifferent; and the fact that the observed differences of reading depend on the direction of rotation removes the possibility of attributing them, small as they are, to ether-drift. It should be noticed, too, that the observation recorded in Section 5 shows a difference of the same order, and that here also it must be due to a cause other than motion through the ether, because rotation is through 180° . In the other sections, with the exception of the second observation in Section 4, the differences are not large enough to justify any meaning being attached to them.

On the whole, therefore, this set of readings points to the conclusion that at no time during the night on which they were taken was there a change of resistance comparable with that looked for. We have, however, been unable up to the present to account for the small spurious effects observed. Several suggestions have presented themselves, but none appears to be valid. It was thought that possibly the twist on the galvanometer arm caused by the rotation might produce a sufficient change of resistance there to effect the small alteration in current. Calculations show, however, that a change of resistance of about 100 per cent. due to twisting copper wire through 90° would be necessary for this to be the case; so that the observed effects cannot be attributed to this cause. A second idea was that the relative change of resistance of the coils was brought about by the alteration of their distribution with respect to the magnetic field in which they stood. That magnetic field, as has been already pointed out, was very small, precautions having been taken to reduce it, as nearly as might be, to zero. This point was tested for by making the field purposely large, in the hope of magnifying the effect; but to no purpose. Finally, a small direct action of the rotating coils on the galvanometer was looked for when a much larger current than usual was passed through them. Here, again, there was no observable effect.

This question must therefore be left undecided. It does not really affect the main aim of these experiments. With regard to this we consider ourselves justified in making the following assertions:—

1. The total electrical resistance of a wire is not altered by an amount exceeding 5×10^{-10} of the whole amount by any change of its position relative to its motion through space.
2. On the assumption that the Fitzgerald-Lorentz shrinkage is a real effect, the specific resistance of a material is dependent upon the direction of flow of the current, being greater to a current flowing parallel to the velocity

of the material through space than to a current in a perpendicular direction. The magnitude of this change of specific resistance is shown by the experiments to be certainly within 2 per cent. of being sufficient to compensate the change of length.

Note.—In view of the very general acceptance of the Fitzgerald-Lorentz shrinkage theory, the negative results of these experiments will probably be attributed to a dependence of specific resistance on direction of current flow. In this connection it is worthy of note that certain independent considerations point to the same conclusion. The electronic theory of metallic conduction leads to the result* that the specific conductivity of a material is measured by the expression

$$\propto \frac{e^2 n}{m} \cdot \frac{\lambda}{v},$$

where n is the number of electrons per unit volume, m the mass of an electron and e the charge upon it, v the mean velocity, λ the mean free path (*i.e.*, the mean distance traversed by an electron between successive collisions with atoms), and α a numerical constant. It is not here of importance whether this expression is absolutely correct or not, provided that it represents the facts dimensionally. The specific resistance is the reciprocal of the above quantity, and we therefore have

$$\rho = \frac{mv}{\alpha ne^2 \lambda}.$$

Of these quantities α and e are independent of the motion through space. The number of electrons per unit volume may also be supposed unaltered by changes of azimuth of the conductor, because the latter has the same volume in all azimuths. The changes of ρ , therefore, depend on the variations of the quantities m , v , and λ . Let us denote by the suffix l the values measured parallel to the drift, and by t the corresponding values in a direction at right angles. Hence,

$$\frac{\rho_t}{\rho_l} = \frac{m_l}{m_t} \cdot \frac{v_l}{v_t} \cdot \frac{\lambda_t}{\lambda_l}. \quad (1)$$

On the shrinkage theory, we expect

$$\lambda_t/\lambda_l = 1 + \frac{1}{2}\beta^2,$$

and, following Lorentz,†

$$m_t/m_l = 1 + \beta^2.$$

* See J. J. Thomson, 'The Corpuscular Theory of Matter,' p. 53.

† 'Amsterdam Acad. Proc.,' 1903-04, p. 809. This value gives complete compensation, while Abraham's value, $m_t/m_l = 1 + \frac{4}{5}\beta^2$, does not. We have consequently taken it in our suggestion of the direction in which to look for the mechanism of compensation.

The only remaining ratio to be determined is v_l/v_t .

Now it is to be expected that the average kinetic energy of the electrons should be independent of the direction of motion; or, in other words, the total kinetic energy associated with any particular direction should be the same. On this assumption we obtain

$$m_l v_l^2 = m_t v_t^2, \quad \text{or} \quad \frac{m_l}{m_t} = \frac{v_t^2}{v_l^2};$$

hence
$$1 + \beta^2 = \frac{v_t^2}{v_l^2}, \quad \text{or} \quad \frac{v_l}{v_t} = 1 - \frac{\beta^2}{2}.$$

Returning to equation (1), it follows that

$$\frac{\rho_l}{\rho_t} = (1 + \beta^2) \left(1 - \frac{\beta^2}{2}\right) \left(1 + \frac{\beta^2}{2}\right) = 1 + \beta^2,$$

since β is a very small quantity.

That is to say, the specific resistance parallel to the ether-drift is greater than that at right angles in the ratio

$$1 + \beta^2 : 1.$$

This corresponds exactly to the conclusions respecting specific resistance arrived at in the experiments above described.

*The Relation between Wind Velocity at 1000 Metres Altitude
and the Surface Pressure Distribution.*

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(Communicated by Dr. W. N. Shaw, F.R.S. Received February 25,—
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For the steady horizontal motion of air along a path whose radius of curvature is r , we may write directly the equation

$$\frac{(\omega r \sin \lambda + v)^2}{r} = \frac{1}{\rho} \frac{\partial p}{\partial r} + \frac{(\omega r \sin \lambda)^2}{r},$$

expressing the fact that the part of the centrifugal force arising from the motion of the wind is balanced by the effective gradient of pressure.

In the equation p is atmospheric pressure, ρ density, v velocity of moving air, λ is latitude, and ω is the angular velocity of the earth about its axis.

If $\partial p / \partial r$ be negative, it is clear that v and $\omega r \sin \lambda$ must have opposite signs: or, for motion in a path concave towards the higher pressure, the air must rotate in a clockwise direction, the well-known result for anticyclonic motion.

Further, the maximum numerical value of $\frac{1}{\rho} \frac{\partial p}{\partial r}$ is $\frac{(\omega r \sin \lambda)^2}{r}$ and the

corresponding maximum value for v is $\omega r \sin \lambda$. Therefore, in anticyclonic regions there are limiting values which the gradient and the velocity cannot exceed. This limiting value of v for latitude 50° and $r=100$ miles is approximately 20 miles per hour.

At the surface of the earth, owing to friction and eddies, the mean direction of the motion of the air is nearly always inclined to the isobars; but over the sea the inclination is very much less, and it seemed probable that in the upper regions of the atmosphere, if the motion were steady, the air would in general move tangentially to the isobars, and its velocity would agree with that calculated from the equation given above.

The question, however, arises as to whether the pressure is likely to continue steady long enough for a condition in which the equation is applicable to supervene. We can get an idea of the time that would elapse before air, starting from rest, would reach a state of steady motion, by considering the motion of a particle on the earth's surface (1) under a constant force in a constant direction, corresponding to straight isobars; (2) under a constant radial force corresponding to cyclonic and anticyclonic conditions. The particle would begin to move at right angles to the isobars in the

direction of the force, but as its velocity increased it would be deflected by the effect of the earth's rotation until it moved perpendicularly to the force.

The equations of motion of a particle, referred to axes fixed relatively to the earth and having an origin on the surface in latitude λ , are

$$\frac{d^2x}{dt^2} - 2\omega \cos \lambda \frac{dz}{dt} - 2\omega \sin \lambda \frac{dy}{dt} = X,$$

$$\frac{d^2y}{dt^2} + 2\omega \sin \lambda \frac{dx}{dt} = Y,$$

$$\frac{d^2z}{dt^2} + 2\omega \cos \lambda \frac{dz}{dt} = Z,$$

where the axis of z is vertical and the axes of x and y are west and south respectively.

If there is no vertical motion we may write the first two equations

$$\frac{d^2x}{dt^2} - a \frac{dy}{dt} = X, \quad \frac{d^2y}{dt^2} + a \frac{dx}{dt} = Y,$$

and the form of the equations and the value of a are unaltered by changing to other axes in the same plane. Let us take the y axis to be in the direction of the constant force b . Then

$$\frac{d^2x}{dt^2} - a \frac{dy}{dt} = 0, \quad \frac{d^2y}{dt^2} + a \frac{dx}{dt} = b,$$

whence
$$x = \frac{b}{a^2}(at - \sin at), \quad y = \frac{b}{a^2}(1 - \cos at),$$

if the particle start from rest. The motion is therefore oscillatory, and the particle moves in a series of cycloidal-like curves, fig. 1. The times to the successive intersections with $y=b/a^2$ are $\pi/2a$, $3\pi/2a$, etc. For latitude 50°

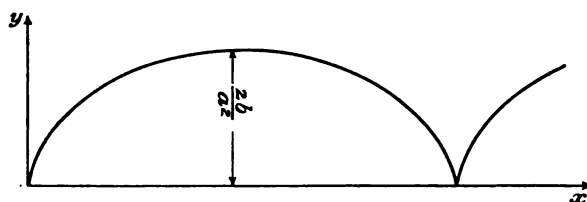


FIG. 1.

these are about 4 and 12 hours. They are independent of b . If there is damping, the motion will be as in fig. 2. If the motion is resisted by a force kv proportional to the velocity, the path will be inclined to the x -axis. Fig. 3 gives the path for the particular case $k=a$ and for a period of time equal to $2\pi/a$, or 16 hours.



FIG. 2.



FIG. 3.

In the case of a constant radial force we have for the motion

$$\frac{d^2 r}{dt^2} - r \left(\frac{d\theta}{dt} \right)^2 = R + ar \frac{d\theta}{dt},$$

$$r \frac{d^2 \theta}{dt^2} + 2 \frac{dr}{dt} \frac{d\theta}{dt} + a \frac{dr}{dt} = 0,$$

whence

$$r^2 \frac{d\theta}{dt} + \frac{1}{2} ar^2 = B.$$

If the particle start from the centre,

$$B = 0 \quad \text{and} \quad \frac{d\theta}{dt} = -\frac{1}{2}a,$$

and we obtain
$$r = \frac{4R}{a^2} (1 - \cos \frac{1}{2}at) = \frac{4R}{a^2} (1 - \cos \theta).$$

The particle therefore describes a cardioid, but if there is damping the motion will come to be along the circle $r = 4R/a^2$.

The time to reach the circle is π/a , or about 8 hours for latitude 50° .

These times are not large meteorologically, and we may therefore expect the relation between air velocity and pressure gradient to be that corresponding to steady motion so long as there are no irregularities to produce turbulent motion.

For application to wind velocities in the upper air we require to know the upper-air isobars. If we have air in which the horizontal layers are isothermal, then from the equations

$$dp = -g\rho dz, \quad p = gk\rho T,$$

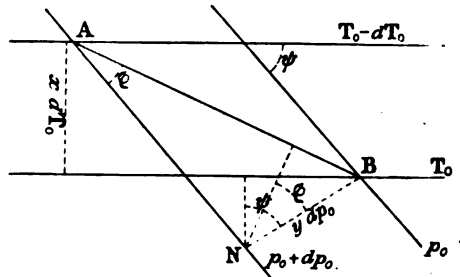
it follows that

$$\log \frac{p_0}{p_z} = \int_0^z \frac{dz}{kT}.$$

We have, therefore, if p_0 and $p_0 + dp_0$ are surface isobars and p_z and $p_z + dp_z$ the corresponding upper isobars,

$$\frac{dp_z}{p_z} = \frac{dp_0}{p_0}, \text{ so that } \frac{dp_z}{\rho_z} = \frac{dp_0}{\rho_0} \frac{T_z}{T_0}.$$

Therefore the velocity calculated from the surface isobars will apply to the upper air, except for the factor T_z/T_0 . For $z = 1000$ metres the effect of this factor is to diminish the velocity by about 2 per cent.



If the conditions are not isothermal, but such that the isotherms and isobars intersect at an angle ψ , the upper isobars will have a different direction from the surface isobars, and the value of the upper gradient will also be changed.

The pressure at a height z above B, the point of intersection of p_0 , T_0 , is $p_0 e^{-z/kT_0}$, and above A, the point of intersection of $p_0 + dp_0$, $T_0 - dT_0$, is

$$(p_0 + dp_0) e^{-z/k(T_0 - dT_0)}.$$

If we assume the vertical temperature gradient to be the same over all the region considered, dT will be the same for every element of the above integral, and we can put $dT_m = dT_0$.

If these two pressures at height z are equal, we must have

$$p_0 e^{-z/kT_0} = (p_0 + dp_0) e^{-z/k(T_0 - dT_0)},$$

or
$$\frac{dp_0}{p_0} = \frac{z}{k} \frac{dT_0}{T_0^2}, \text{ or } \frac{dp_0}{\rho_0} = gz \frac{T_0 dT_0}{T_0^3}.$$

In this case AB is the direction of the upper isobar and its inclination ϕ to the lower isobar is given by

$$\tan \phi = \frac{y dp_0}{x dT_0 \operatorname{cosec} \psi + y dp_0 \cot \psi},$$

where $x dT_0$ and $y dp_0$ are the distances between the isotherms and isobars.

Substituting for dT_0 and dividing out by dp_0 , we get

$$\cot \phi = \cot \psi + \frac{x}{y} \frac{T_0^2}{g \rho_0 z T_0} \operatorname{cosec} \psi.$$

Taking y and x for millimetre isobars and 1° C. isotherms and putting $z = 1000$ metres and $T_m^2/T_0 = 2T_m - T_0 = 270^\circ$ C., say, we find

$$\cot \phi = \cot \psi + 2.8 \frac{x}{y} \operatorname{cosec} \psi.$$

To obtain the upper pressure gradient, we consider the upper isobars over B and N. The difference of temperature between B and N is $y/x \cdot dp_0 \cos \psi = dt$, say.

Therefore the upper pressure difference is

$$\begin{aligned} (p_0 + dp_0) e^{-z/k(T_m + dt)} - p_0 e^{-z/kT_m} &= e^{-z/kT_m} \left[dp_0 + \frac{p_0 z dt}{kT_m^2} \right] \\ &= p_0 e^{-z/kT_m} \left[1 + \frac{p_0 z \cdot y \cos \psi}{x k T_m^2} \right]. \end{aligned}$$

The distance between these isobars is $y dp_0 \cos \phi$ and the upper gradient is consequently

$$\frac{1}{y \cos \phi} e^{-z/kT_m} \left[1 + \frac{p_0 z y \cos \psi}{x k T_m^2} \right] = \frac{1}{y \cos \phi} e^{-z/kT_m} \left[1 + \frac{g \rho_0 z T_0}{T_m^2} \frac{y \cos \psi}{x} \right],$$

and the ratio $\frac{1}{\rho_z} \frac{\partial p_z}{\partial r} / \frac{1}{\rho_0} \frac{\partial p_0}{\partial r}$ is $\sec \phi \left[1 + \frac{g \rho_0 z T_0}{T_m^2} \frac{y \cos \psi}{x} \right] \frac{T_z}{T_0}$,

which is $g \rho z \operatorname{cosec} \phi \cdot \frac{y \sin \psi}{x}$, taking T_z/T_0 to be unity, namely,

$$\operatorname{cosec} \phi \cdot \frac{1}{\cot \phi - \cot \psi} \quad \text{or} \quad \frac{\sin \psi}{\sin (\psi - \phi)}.$$

In the special cases, $\psi = 0$ or 180° , the ratios are

$$\left(1 \pm \frac{g \rho_0 z}{T} \cdot \frac{y}{x} \right) \quad \text{or} \quad \left(1 \pm \frac{y}{2.8x} \right), \text{ for } z = 1000 \text{ metres.}$$

If $x = 2y$, which would represent a possible case, the increase or decrease would be about 18 per cent.

For $\phi = \frac{1}{2}\pi$ the rotation would in the same circumstances be about 10° .

During the year 1905 a series of observations in the upper air was made at Berlin and Lindenberg, near the time of the general 8 A.M. morning observations. It was therefore possible to compare the wind velocities observed with those calculated from measurements of the gradient by the use of the formula at the beginning of this paper, the motion being assumed tangential to the isobars.

For purposes of calculation the formula may be written

$$v(1 \pm 0.00108 v \cot \psi \operatorname{cosec} \lambda) = \frac{709 \operatorname{cosec} \lambda}{x} \frac{T}{T_0} \frac{B_0}{B},$$

where ψ is the angular radius of the small circle, on the earth's surface,

osculating the path, v is in metres per second, x is the distance in kilometres between millimetre isobars, T , B are the temperature and pressure, and T_0 , B_0 the corresponding values for air at 0° C. and 760 mm.

If the motion is along straight lines, $\cot \psi = 0$, and the values of v for $B = B_0$, $T = T_0$, are as follows if $x = 50$ kilometres.

| | | | | | |
|----------------|------------|------------|------------|------------|------------|
| Latitude | 30° | 40° | 50° | 60° | 70° |
| v | 28.4 | 22.1 | 18.5 | 16.4 | 15.1 |

If v_0 represent the velocity when $\cot \psi = 0$, we can most easily express the solutions of the equation for different values of ψ , x , λ , by taking as independent variables, ψ , v_0 , λ .

Taking, as an example of the dependence on ψ , $\lambda = 50^\circ$, $v_0 = 40$ metres per second, we obtain the following values for v in metres per second in the case of cyclonic motion.

| | | | | | | | | | | |
|--------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|------------|
| ψ | 1° | 2° | 3° | 4° | 5° | 6° | 7° | 8° | 9° | 10° |
| v | 17 | 21 | 24 | 26 | 28 | 29 | 30 | 31 | 31 | 32 |

For anticyclonic motion the gradient corresponding to $v_0 = 40$ metres per second is above the maximum, and we take for two examples $v_0 = 12$, 30 metres per second.

The values of v are then as follows for the two cases :—

| | | | | | | | | | | | |
|----------------------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-------------|
| | ψ . | 1° | 2° | 3° | 4° | 5° | 6° | 7° | 8° | 9° | 10° |
| For $v_0 = 12$ | $v =$ | — | — | — | 20 | 16 | 15 | 14 | 14 | 14 | 13 m. p. s. |
| For $v_0 = 30$ | $v =$ | — | — | — | — | — | — | — | — | — | 50 „ |

Where no value is inserted for v , the gradient corresponding to the given value of v_0 is above the maximum for the corresponding value of ψ .

To show the dependence on λ , we take $\psi = 3^\circ$, and put $v_0 = 40$ metres per second for cyclonic motion, and $v_0 = 10$, 5 metres per second for anticyclonic motion. The following table gives the values of v for different latitudes in the three cases :—

| | | | | | | |
|----------------------|-------------|------------|------------|------------|------------|-------------|
| | λ . | 30° | 40° | 50° | 60° | 70° |
| For $v_0 = 40$ | $v =$ | 21 | 23 | 24 | 25 | 26 m. p. s. |
| For $v_0 = 10$ | $v =$ | — | — | — | 17 | 15 „ |
| For $v_0 = 5$ | $v =$ | 7.1 | 6.3 | 6.0 | 5.8 | 5.7 „ |

By the use of tables giving values of v_0 for different values of x , T , B , and of v for different values of λ , v_0 , ψ , each wind observation at 1000 metres altitude was compared with the value deduced from the surface isobars. The temperature correction was not applied.

The following table gives the result of the comparisons :—

Comparison between Barometric Gradient Wind and Observed Wind at 1000 Metres Altitude for the Year 1905
(Berlin and Lindenbergl).

Table of Averages.

| | Theoretical velocity v . m.p.s. | Velocity v_1 at 1000 metres. m.p.s. | Percentage difference between v and v_1 . | Mean deviation in points of v_1 from v (+ when v_1 veers from v). | Mean surface wind. m.p.s. | Mean deviation in points of wind v_1 from surface wind. | Surface wind \pm v cosine (deviation). | Wind at 1000 metres $\pm v_1$ cosine (deviation). | Component wind \perp to isobars at surface + component at 1000 metres. |
|----------------|---|--|--|--|------------------------------------|--|---|--|--|
| Berlin. | | | | | | | | | |
| January..... | 15.7 | 15.1 | 4.0 | -0.6 | 5.0 | 3.3 | 0.45 | 0.97 | 1.9 |
| February..... | 12.0 | 11.6 | 3.5 | -0.6 | 4.0 | 2.7 | 0.41 | 0.98 | 1.7 |
| March..... | 8.1 | 6.6 | 23.0 | -0.4 | 2.6 | 1.7 | 0.35 | 0.82 | 1.9 |
| Lindenbergl. | | | | | | | | | |
| April..... | 10.2 | 8.8 | 16.0 | -1.0 | 4.8 | 1.7 | 0.54 | 0.90 | 1.4 |
| May..... | 8.3 | 6.5 | 28.0 | -1.0 | 4.5 | 2.3 | 0.65 | 0.80 | 1.9 |
| June..... | 6.8 | 6.4 | 6.0 | -0.5 | 3.9 | 1.1 | 0.60 | 0.95 | 1.9 |
| July..... | 8.4 | 8.2 | 2.4 | -0.9 | 4.5 | 1.2 | 0.68 | 1.0 | 1.3 |
| August..... | 8.9 | 8.0 | 11.0 | -0.9 | 5.1 | 1.6 | 0.64 | 0.92 | 1.6 |
| September..... | 10.3 | 10.5 | -2.0 | -0.8 | 5.4 | 2.2 | 0.63 | 1.03 | 1.6 |
| October..... | 12.1 | 11.9 | 2.0 | -0.5 | 6.3 | 2.7 | 0.64 | 0.99 | 2.7 |
| November..... | 10.6 | 10.1 | 5.0 | -0.9 | 5.9 | 3.1 | 0.78 | 0.97 | 2.3 |
| December..... | 11.0 | 10.3 | 7.0 | +0.3 | 5.5 | 3.9 | 0.65 | 0.94 | -5.? |
| Summer..... | 8.8 | 8.1 | 8.5 | -0.8 | 4.7 | 1.7 | — | 0.93 | — |
| Winter..... | 11.6 | 10.9 | 6.5 | -0.45 | 4.9 | 2.9 | — | 0.95 | — |
| Year..... | 10.2 | 9.5 | 7.5 | -0.6 | 4.8 | 2.3 | — | 0.94 | — |

The upper wind coincides in direction very nearly with the isobars at the surface, and the wind velocity observed agrees well with that calculated from the pressure distribution. The differences are not greater than possible errors of observation, except in spring.

It is known that the upper wind always veers from the surface wind, and the numbers in Column 7 show that in 1905 the veering was considerably greater in winter than in summer.

If the effect of the earth's surface were the same as if a frictional force opposed the motion, the relation between the wind and gradient of pressure would be as above, except that the effective gradient would be the maximum gradient multiplied by the cosine of α , the angle between the path and the isobars. The corresponding velocity would be approximately $v \cos \alpha$, except in cases of considerable curvature. In the majority of the observations the curvature was small, and we should therefore expect the surface wind to be nearly $v \cos \alpha$, so that the numbers in Column 8 would be nearly unity. This is far from being the case; but the change of the station of observation from Berlin to Lindenberg is accompanied by a corresponding change in the ratio of the surface wind velocity to $v \cos \alpha$.

This suggests that the effect of the surface, apart from the purely frictional effect, is to reduce the velocity in a given direction in a constant ratio depending on the locality, and that departures in the observed velocities from those corresponding to this ratio are to be associated with unsteady meteorological conditions.

The last column gives approximately the ratio of the volume of air crossing the isobars at the surface to the volume crossing at 1000 metres.

The ratio appears to be nearly constant; the change in December is probably due to the exceptional conditions which prevailed during part of the month, when the air was considerably warmer at 1000 metres altitude than at the surface.

On the Polymorphic Changes of Ammonium Nitrate.

By U. BEHN, Harling Fellow of the University of Manchester.

(Communicated by Arthur Schuster, F.R.S. Received and read June 27, 1907,—
Received in revised form January 29, 1908.)

As has been shown by the extensive investigation of Tammann, polymorphic changes occur far more frequently than is supposed. Among substances which exhibit these phenomena, ammonium nitrate serves as a specially interesting example. Not only does this compound undergo four distinct transformations within a range of 150° , but the remarkable nature of the changes possesses a special interest.

The various modifications of ammonium nitrate have been studied repeatedly. The crystallography by Frankenheim (1854), O. Lehmann,* Wyruboff,† and Wallerant,‡ the general physical properties by Bellati and Romanese,§ S. Lussana, and recently by Tammann|| (1902).

The melting point of the salt is about $+166^{\circ}$.¶ At this temperature it solidifies in crystals of the cubic system (modification I). At $+126^{\circ}$ the first transformation takes place, the substance becoming doubly refractive (+) and the crystals being now tetragonal. This modification (II) is stable down to $+83^{\circ}$, at which temperature a second change occurs, optically biaxial crystals of the monosymmetric system being formed. These crystals have an almost tetragonal appearance, "monocliniques quasi-quadratiques" (Wallerant).

A further transformation occurs at 32° , orthorhombic ("quasi-quadratiques") crystals being formed. This modification (IV) is stable at ordinary temperatures, and is consequently the best known. The parameters are $1.167:1:0.736$.

A fourth transformation occurring at -16° ** was first observed by Lehmann. The modification (V) produced at this temperature is again

* 'Molekularphysik.'

† Probably 'Bull. Soc. Min. de France.'

‡ 'Comptes Rendus,' vol. 142, 1906.

§ 'Atti del Istit. Veneto' (6), vol. 4, 1886.

|| 'Annalen der Physik,' vol. 7, p. 223, 1902.

¶ H. Schiff and U. Monsacchi, 'Zeit. für Phys. Chem.,' vol. 21, p. 2, 1896; 168° according to Bellati and Romanese; 161° according to O. Lehmann, 'Ann. der Physik,' vol. 21, p. 181, 1906.

** According to a private communication from Lehmann, his first assertion that the point of transition was -4° was founded on a mistake, the observations proving the temperature to be -16° .

tetragonal, and has a double refractive (+) power a little weaker than that of the modification II. The general similarities of the two modifications induced Wallerant to suggest that they were identical.* The reasons given for this supposition will be discussed in the crystallographic section of the paper, but it must be remarked that Wallerant seems scarcely to have realised that such a fact as this, if it could be proved, would be quite unique and possess very great importance. The phenomenon of the miscibility of nicotine and water within two ranges of temperature, which he quotes as an analogy, is certainly quite a different case, for here one single physical property is the same, whereas with these crystals it is a question whether the same form with all the physical properties identical can exist within two separate ranges of temperature.

In the following investigation an attempt has been made to attack this problem from several directions. First, the volumes of the two modifications were studied and compared; then the thermal properties were investigated, and finally the crystallographic side of the question was examined.

The salt employed was the purest that could be obtained (Kahlbaum, Berlin). Ten grammes slowly heated in a crucible left 0.05 per cent. residue. As the salt is hygroscopic, special care was taken to obtain it in a dry condition. Since, upon heating, ammonium nitrate decomposes even below its melting point, the dehydration was effected at ordinary temperatures by exposure over phosphorus pentoxide in evacuated desiccators. In this manner it was possible to obtain the salt containing certainly less than 0.1 per cent. of water. I am much indebted to Dr. G. H. Bailey for helpful suggestions on this point.

Absolute freedom from moisture can, however, not be secured. Upon opening a desiccator which had been standing for a few days, a strong smell of oxides of nitrogen was observed, the decomposition occurring more rapidly at higher temperatures. If, for instance, the salt be placed in a bent glass tube which is evacuated, and one limb be heated to 100° , whilst the other is cooled to -79° ,† water is continuously collected, yet the salt becomes no drier. At 130° the decomposition is still more rapid, especially if turpentine is present, and it is remarkable that this decomposition is accompanied by a decrease in volume. After a dilatometer had been maintained for three hours at temperatures between 100° and 130° , the

* "Il n'y aurait rien de surprenant dans l'existence de deux modifications appartenant au même système et parallèlement orientées. . . . Mais bien plus il n'y a en réalité qu'une modification stable dans deux intervalles de température."

† The temperatures of solid carbonic acid and liquid air are given throughout in round numbers.

meniscus fell 26 mm., and the next day upon exposure to low temperatures the bulb of the instrument burst, evidently on account of the formation of ice. It is worthy of note that the salt, which after the heating had a brownish appearance, showed no trace of nitrite when analysed (Bailey). These observations indicate that the dilatometer should be employed first for the low-temperature readings and, subsequently, for the higher temperatures, and should not afterwards be used again. Even during the filling of the dilatometer it is necessary to avoid as far as possible any excessive heating. Provided these precautions are strictly observed, the salt remains perfectly white, and no sign of decomposition can be detected.

The dilatometers employed had the form and size of those used by van't Hoff,* with the slight modification that the bulb used for filling was sealed to the capillary tube instead of being connected by a cork. A measured quantity of the dry salt was placed in the narrow cylindrical tube of the dilatometer, which was then sealed off and the liquid was drawn in from the other end by means of an air pump.

Pure turpentine† was used for this purpose and it has the advantage of remaining liquid throughout the whole range of temperature required. In some few experiments xylol was employed. During the filling, the turpentine was allowed to boil at comparatively low temperatures, while the upper bulb was surrounded by solid carbonic acid to prevent turpentine vapour from escaping from the dilatometer and thus changing the composition of the liquid.

After a few preliminary experiments with dilatometers constructed of ordinary glass, resource was had to thermometer glass, "Jena 59," which, as is well known, possesses an extremely small secular change, and is also in other respects regular in its behaviour.

The bulb of the dilatometer was immersed in a bath of turpentine in an unsilvered Dewar vacuum cylinder. This bath was heated electrically by means of a short nickel wire spiral lying at the bottom of the vessel, and cooled either with water flowing through a suitably bent tube, or, for temperatures below 0° , with solid carbonic acid thrown in small quantities into the turpentine. The bath was continually stirred by a revolving stirrer of the ordinary type (fig. 1); with this arrangement the temperature was maintained constant to $1/10^{\circ}$ at any point between -70° and (say) 130° .

The temperature was measured below -30° by a pentane thermometer, at higher temperatures by a mercury thermometer,‡ both made of "Jena 59"

* 'Zeit. für phys. Chemie,' vol. 17, p. 50, 1895.

† Woolley and Sons, Manchester.

‡ Both constructed by the firm of C. Richter, Berlin.

glass and calibrated at the Physikalisch-Technische Reichsanstalt of Berlin. Both thermometers were completely immersed in the turpentine of the bath.

Since the dilatometers had a length of about 70 cm., it was not convenient to completely immerse them, and their readings had consequently to be corrected for that portion of the capillary which was exposed.

Preparatory to the experiments with the salt, the behaviour of the turpentine was carefully examined. Its specific gravity was 0.865 at 18°, which was identical with that of another specimen obtained from Merck, of Darmstadt; the boiling point was 155°; it became very viscous at -130° and froze, as an apparently crystalline substance, with contraction, at a slightly lower temperature.

The turpentine was practically free from water, as was proved by the following experiment:—Two hundred grammes of the liquid were put into a calorimeter, together with a thin glass bulb containing several grammes of ammonium nitrate, and a second bulb containing 1 gramme of water. The temperature of the apparatus was allowed to become constant at 16°.020. Upon breaking the bulb containing the salt no change of temperature could be detected ($16^{\circ}.020 \pm 0.005$), but after the second bulb had been broken the temperature fell within one minute to 15°.470. This result was confirmed and seems to indicate that the turpentine contained less than 0.005 per cent. of water.

The dilatation, measured in the apparatus previously described, gives an almost linear curve, the apparent expansion increasing slightly with temperature. From this curve the following values of the volumes (corrected) are deduced, the volume at 0° = 1, 100° = 1.104, 30° = 1.029, -40° = 0.966, and hence $v = v_0 (1 + \alpha t + \beta t^2 + \gamma t^3)$, $\alpha = 0.000922$, $\beta = 0.00000163$, $\gamma = -0.0000000045$.

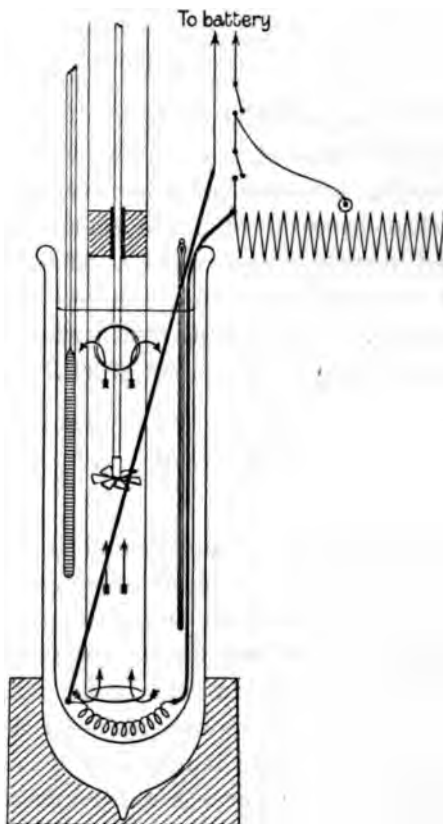


FIG. 1.

Thus the real coefficient of expansion at

$$\begin{array}{ll}
 -60^{\circ} = 0.000677 & +20^{\circ} = 0.000982 \\
 -20^{\circ} = 0.000852 & +60^{\circ} = 0.001069 \\
 0^{\circ} = 0.000920 & +100^{\circ} = 0.001113 \\
 +18^{\circ} = 0.000978 &
 \end{array}$$

The values found by Kopp (1855) and by Bellati and Romanese for a smaller range of temperature agree reasonably, their values at 20° being 0.000973 and 0.000963 respectively.

The changes in volume of ammonium nitrate were determined by Bellati and Romanese in two cases, at $83^{\circ} - 1.43$ per cent., and at $32^{\circ} + 3.30$ per cent. It seemed of interest to make this determination for all four polymorphic changes. The following results were obtained, the volumes being compared with the volume of the salt at 20° .

$$\begin{array}{ll}
 +126^{\circ} & +2.3 \text{ per cent.} \\
 +83^{\circ} & -1.4 \text{ " } \\
 +32^{\circ} & +3.8 \text{ per cent.} \\
 -18^{\circ} & \left\{ \begin{array}{l} -2.6 \text{ " } \\ -3.1 \text{ " } \end{array} \right.
 \end{array}$$

The individual observations differ, except in the change at -18° , less than 0.2 from one another. As can be seen, the changes in volume are considerable in magnitude, alternately an increase and a decrease being noted. The specific gravity at $+20^{\circ}$ was found to be 1.725.

Regarding the last value in the table, some uncertainty was caused by the fact that after the fourth transformation the meniscus would slowly rise for hours, although the temperature of the dilatometer was kept constant. After proving that this change was not due to any secular change in the glass, nor to any semi-permanent change in the turpentine, it was shown that it can be accounted for by the slowness of the transformation. After cooling to about -50° for at least 12 hours, the meniscus behaved quite regularly; but on returning, after cooling, to the standard temperature ($+18^{\circ}$) the new position of the meniscus was always sensibly (up to 0.5 per cent.) higher than before. The correct explanation of this anomalous behaviour seems to be that part of the changed salt will remain in this modification, even if heated to $+18^{\circ}$; a fact which was at first considered improbable, but which is corroborated by the behaviour of the salt at low temperatures. (*Cf.* crystallographic section.) This uncertainty is indicated in figs. 2 and 2A.

The chief point at issue is the relation between the volumes of the two tetragonal modifications. Fig. 2 shows four curves determined with different dilatometers, the readings for these being uncorrected.

Observations were made at -60° , -50° , -40° , -30° , -20° , and also at

+120° and +110° (these not always), +100°, +90°, +80°, +70°, +60°, +50°. The tetragonal modification ceases to be stable at +83°, but it could easily be cooled to +45°, at which temperature the change generally took place. If one compares this observation with the temperature-pressure curve of Tammann,* it is seen that this is the temperature at which the change between the modifications II and IV takes place at ordinary pressure. In all probability the transformation starts in this way, although the actual product observed is III.

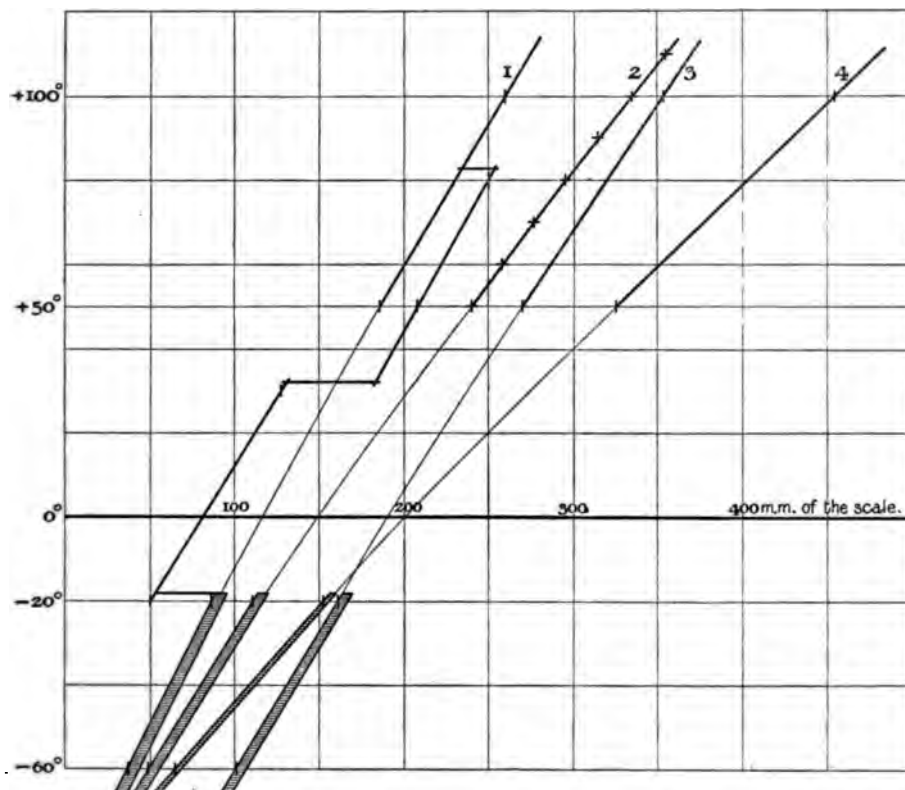


FIG. 2.

According to Wallerant, modification III can be suppressed altogether whilst cooling, either by a small addition of caesium nitrate or by pressure, this transformation product having a larger specific volume than either of the neighbouring modifications.

From the curves in fig. 2† it appears that the two parts might be connected

Loc. cit.

† The limit of error is about 1 mm. Greater accuracy would be possible, but for the difficulty of estimating the temperature of the exposed stem of the dilatometer.

by a reasonably smooth curve; yet the curvature of the connecting link is greater than that of the observed parts. From these experiments no conclusion contradicting the identity of the two modifications II and V can be arrived at.

In fig. 2A the dilatation of the turpentine is eliminated, and the changes of volume of the salt are thus more clearly indicated.

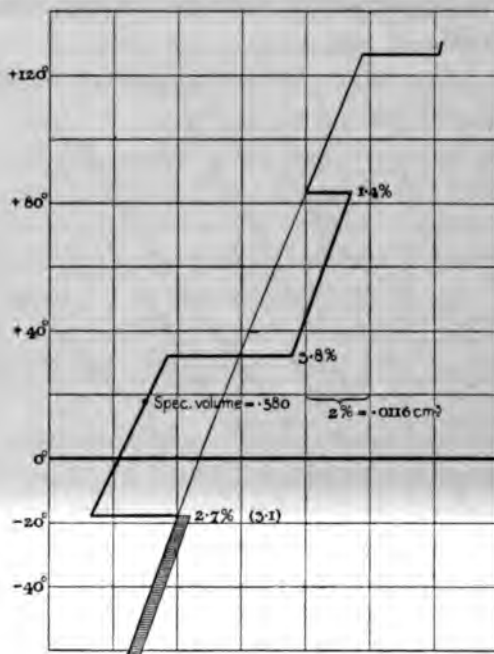


FIG. 2A.

The temperature at which the fourth change occurs, given by other authors as -16° , was determined by van't Hoff's method.* After about half the salt had been transformed, the temperature was maintained constant at -14° , -16° , -18° , and -20° , and readings of the dilatometer were taken. The slowness of the change precludes great accuracy, but the most probable value appears to be -18° .

For the calorimetric work, the method of mixtures was employed. Measurements were made of the specific heats above and below the point of transition, -18° , and also of the heat of transformation. The liquid chosen for the calorimeter was again pure turpentine. The salt was filled into cartridges of tin foil,† this material, which can easily be broken open in the

* 'Vorlesungen über theoret. u. physik. Chemie,' vol. 1, p. 18, 1898.

† The tin foil was rolled in several thicknesses, bright side outwards, on a hollow wooden cylinder; it was folded at the bottom and the cartridge thus formed was blown

calorimeter, proving satisfactory for the protection of the salt from atmospheric moisture.

A long introductory series of experiments proved quite useless, the results being discordant. The explanation was found in the dilatometric observations just described. Once the discovery was made that it is necessary to cool the salt for at least twelve hours in order to complete the transformation, no difficulties were met with. The methods were similar to those previously employed.* The turpentine was ordered in two large consignments to ensure uniformity, and care was taken to use each portion of it only once. For the temperature readings a thermometer of Jena glass 59 and of small range was employed; this instrument was twice calibrated at the Physik.-techn. Reichsanstalt, at Charlottenburg.

The specific heat of the turpentine at ordinary temperatures ($+16^{\circ}$) was found in several experiments to be: 0.425, 0.422, 0.420, 0.424; mean, 0.423. Since it appeared to rise slightly when the material was exposed to the air, the value 0.425 was employed.

1. The measurements of the specific heat of ammonium nitrate between -15° and $+15^{\circ}$ gave 0.387, 0.397, 0.391, 0.399; mean, 0.395. For these experiments the salt was kept at -15° , care being taken not to let the temperature fall during the whole process below this point; during the last half hour the temperature was kept constant between $-14^{\circ}8$ and $-15^{\circ}2$.

2. The heat absorbed when the salt was heated from -20° to $+15^{\circ}$ enabled the heat of transformation to be calculated.† Individual results gave 1.64, 1.58, 1.61; mean, 1.62.

In these experiments the samples were first maintained for at least twelve hours at -79° and then heated to -20° , which temperature towards the latter part of the process was kept constant within $\pm 0^{\circ}2$.

3. For the interval -79° to -20° the specific heat was determined, 0.351, 0.352, 0.354; mean, 0.352.

For the interval between $-190^{\circ}\ddagger$ and ordinary temperature the value of

off the cylinder. Then a tin-foil disc of suitable size was dropped into the cartridge, which, after weighing, was filled with salt and closed by twisting the tin foil at the upper end.

* U. Behn, 'Annalen der Physik,' vol. 1, p. 257, 1900.

† *E.g.*, 39.62 grammes salt in 3 grammes tin foil. Turpentine in calorimeter, 270.8 grammes. Rise of temperature in calorimeter, $4^{\circ}715$. Rise of temperature of salt and tin foil, $33^{\circ}3$. Water equivalent of calorimeter, 10.45.

$$39.62 \times 33.3 \times 0.395 + 39.62 \times q + 3.0 \times 33.3 \times 0.05 = 270.8 \times 4.715 \times 0.425 + 10.45 \times 4.715.$$

Hence

$$q = 1.64.$$

‡ Approximate, as measured by pentane thermometer.

the specific heat proved to be 0.311, 0.307, 0.302;* mean, 0.305. Hence for the interval -190° to -20° the specific heat may be taken as 0.274. *

Taking this latter value and that of 3, the real specific heat within the range may be expressed

$$S_5 = a + bt, \text{ where } a = 0.423 \text{ and } b = 0.00143.$$

In a similar manner, taking the value of Bellati and Romanese for S_4 between 0° and $31^{\circ} = 0.407$, and the value given in 1, we can express

$$S_4 = a + bt, \text{ where } a = 0.395 \text{ and } b = 0.00075.$$

In addition, we have the values determined by Bellati and Romanese: $S_2 = 0.426$, $S_3 = 0.355$, and $S_4 = 0.407$ (between 0° and 31°), and the heats of transformation at $83^{\circ} = 5.33$, and at $32^{\circ} = 5.02$.

If it were thermodynamically possible that the two tetragonal modifications were identical, we should have, as pointed out previously, the unprecedented instance of a single definite substance being stable within two distinct ranges of temperature. Then we might perform the following reversible cycle (*cf.* fig. 3). Transform 1 gramme of ammonium nitrate at $+83^{\circ}$ into the modification III, stable below this temperature; let this cool to 32° ; here transform to modification IV and cool to slightly below -18° , and finally

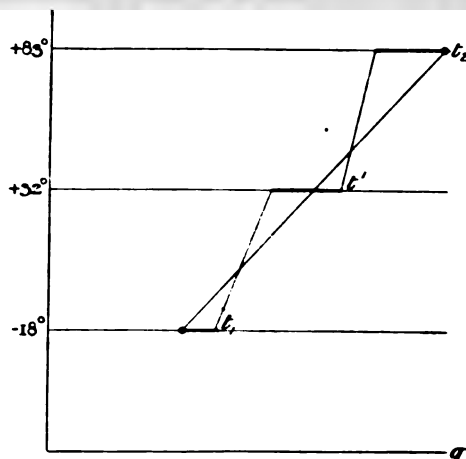


FIG. 3.

heat this, after the transformation to modification V, again to 83° (this latter part of the circuit is unstable and hence can probably only be theoretically accomplished).

* The last value due to a more carefully conducted experiment is given double value in the estimation.

This series of changes produces Q_2 calories at $+83^\circ$ (t_2), Q' calories at $+32^\circ$ (t'), and Q_1 calories at -18° (t_1). The specific heats of the modifications in the order mentioned above are S_3 , S_4 , and S_5 .

$$\text{Then we have} \quad Q_2 + \int_{t'}^{t_2} S_3 dt + Q' + \int_{t_1}^{t'} S_4 dt + Q_1 = \int_{t_1}^{t_2} S_5 dt.$$

It would be wrong to suppose that the identity of II and V involves the vanishing of the sums of the heats of transition. This could only be the case if

$$\int_{t'}^{t_2} S_3 dt + \int_{t_1}^{t'} S_4 dt = \int_{t_1}^{t_2} S_5 dt,$$

as we should have in that case

$$Q_2 + Q' + Q_1 = 0.$$

This would necessitate that each of the heats of transition should be zero, since, according to van't Hoff's law of movable equilibrium, none of them can be negative.

Unfortunately, we can only give a very rough estimate of S_5 between -18° and $+83^\circ$. Supposing that this quantity alters as a linear function of the temperature, we should find the average specific heat -18° and $+83^\circ$ to be 0.397. But, on the other hand, supposing the modifications V and II to be identical, we might employ the value determined by Bellati and Romanese between 83° and 125° , viz., 0.426. From which $S = a + bt + ct^2$ (where $a = 0.397$, $b = 0.000684$, $c = -0.00000383$), and thus obtain the mean value of S to be 0.412 between -18° and 83° .

Assuming the latter value to be correct, the above equation would lead to—

$$5.3 + 51 \times 0.355 + 5.0 + 50 \times 0.401 + 1.6 = 101 \times 0.412,$$

$$\text{i.e., } 50.0 = 41.6.$$

Although slight errors in the specific heats might cause an appreciable change in the numerical values of the two sides of the equation, it seems hardly possible that so great a difference as 8.4 could be due to errors of observation.

It follows from the considerations of the above numbers that if the modifications II and V are identical, its average specific heat between the temperatures -18° and $+83^\circ$ would have to be considerably higher than at either of these two temperatures. So far as this argument goes it tells against the identity, but it is not decisive.

According to the kinetic theory of Richarz* for allotropic elements, the specific heat will be large when the density is small, and *vice versa*. Wigand† has recently applied this rule to compounds, but Richarz himself has not supported this extension of his rule, and, indeed, one must use extreme caution before applying such relations to complicated cases.

The specific heats of salts, and amongst them of ammonium nitrate, have recently formed the subject of a research by Forch and Nordmeyer.‡ The method they adopted is similar to that employed for the determination of the heat of evaporation of liquid air.§

Since the value found by these investigations, 0.254 for ammonium nitrate, does not agree at all well with that given above, 0.303 ± 0.003 , it was thought advisable to repeat the determinations by this method.

After obtaining satisfactory values of the specific heat of brass, aluminium, and "Jena 59" glass, measurements were made with ammonium nitrate. These experiments yielded a value 0.294, whilst a sample of the same salt, measured in the ordinary calorimeter, immediately afterwards, gave 0.301. These results are in satisfactory agreement; although it seems possible that a fifth change may take place below -18° , which would account for the discrepancy. This change would, however, probably be even slower than that at -18° , and thus be very difficult to detect.

Lehmann|| could detect no such transformation, and, in the present investigation, a dilatometer slowly cooled to -140° , whilst clearly indicating the first four changes, gave no indication of a further transformation.

For the interest of the experimental method, although unsuccessful in the special application, mention may be made of an attempt to determine heats of transformation at -18° . In the case of water, satisfactory measurements were obtained. Ten grammes of water were placed in a zinc cylinder weighing 8 grammes, which was suspended at the centre of a metal box. The latter was maintained at -78° during the cooling period, and at $+37^{\circ}$ during the reheating. Readings of the temperature of the water were taken with an iron-constantan thermo-couple. From the rate of cooling or heating, the number of calories which enter the cylinder every minute can be deduced. The curves plotted for this experiment enable the difference in

* 'Wied. Annalen,' 1893, vol. 48, p. 708, and 1899, vol. 67, p. 704; 'Sitzungsber. Marburger Gesell.,' July, 1904, pp. 64—66.

† 'Annalen der Physik,' vol. 22, p. 64, 1907.

‡ 'Annalen der Physik,' vol. 20, p. 423, 1906.

§ J. Dewar, 'Roy. Instit. Proc.,' vol. 14, p. 398, 1894; U. Behn, 'Annalen der Physik,' vol. 1, p. 270, 1900; J. Dewar, 'Chemical News,' vol. 92, p. 181, 1905.

|| 'Annalen der Physik,' vol. 21, p. 181, 1906.

the specific heat of ice and water to be clearly seen. The values of the latent heat of fusion obtained in this way were 75 and 68, which are reasonably near 74.4, the correct value.

Yet, even with much finer thermojunction wires, a similar experiment with ammonium nitrate proved unsuccessful so far as the transformation V is concerned, obviously on account of the slowness of the change, although all the other changes could be readily located.

Crystallographic Measurements.

Upon the basis of the microscopic examination of ammonium nitrate itself, Wallerant has suggested that the tetragonal forms stable above 83° and below -18° are identical, as is indicated by the following passage from his paper:—"Quand on suit sous le microscope, etc. . . ." Further, by adding various proportions of an isomorphous salt, namely, caesium nitrate, to the ammonium nitrate used, Wallerant was able to show that the tetragonal modification of ammonium nitrate could be rendered stable, not only above 83° and below -18° , but also throughout the whole intermediate range of temperature; the admixture with caesium nitrate thus gave the tetragonal modification stability at temperatures between -18° and 83° . Although the experimental result is striking, it is not conclusive, because, whilst the two tetragonal forms admittedly resemble each other closely, it necessarily remains an open question as to whether a transition from one to the other modification does not occur without obvious physical change.

For these and for other reasons which will at once suggest themselves, it seemed desirable to subject the tetragonal modifications stable above 83° and below -18° to careful crystallographic examination, in order to determine whether they really belong to the same class of the system, or whether morphological differences are traceable between them of such a nature as to indicate a structural dissimilarity.

In the first place, supersaturated solutions of ammonium nitrate were caused to crystallise by slow cooling in unsilvered Dewar vessels; it was found convenient to work in aqueous solutions at about 100° and in dilute alcoholic solutions at about -30° . In each case skeletal crystals were obtained, which exhibited every indication of tetragonal symmetry, but no indications of hemi- or tetarto-hedral symmetry.

The best conditions for the production of well-characterised crystals of the modification stable below -18° are difficult to determine, and ordinarily skeletal crystals, extending only in two directions, are obtainable at this temperature. In some few cases, however, skeletal growths extended in the

three rectangular directions were obtained, and in these the same sort of difference in kind between the nature of the growth in a third direction and that in the other two was observed.

These experiments, whilst clearly indicating the tetragonal symmetry of the crystals, give no indication that the tetragonal modifications stable at the high and the low temperatures are morphologically different.

The microscopic examination of ammonium nitrate at the high and the low temperature in absence of a solvent led to conclusions similar to the foregoing. It was found possible to arrange a sheet of thin platinum foil heated electrically and insulated from the microscope stage in such a manner that the modification stable above 83° could be preserved for any desired period upon a glass slide laid under the platinum sheet; the preparation was examined through a hole cut in the metal foil. The difficulties introduced by the possible deposition of atmospheric moisture upon the modification stable below -18° were overcome by surrounding the portion of the slide under examination by an annular ring of solid carbon dioxide cut by a cork borer from a hammered disc of the substance, the objective being slowly lowered and pressed into the ring; by working in this manner, the constant evolution of carbon dioxide gas prevents the access of atmospheric moisture to the slide and the objective. Both arrangements are very simple, and seem well adapted for the microscopic examination of substances at high and low temperatures.

Wallerant has stated that on passing from the modification stable above 83° to that stable below -18° , with intermediate formation of the modifications stable between these temperatures, the orientation of the two tetragonal individuals is, in general, found to be the same. This could not be confirmed, but it must be mentioned that even if the orientation of the two tetragonal modifications systematically differs, no argument is deducible against the identity of the two modifications, for even the same modification will very often reappear with another orientation after a transformation, especially if the changes occur slowly.

The double refraction figure of modification III seemed regularly to appear in the place of the uniaxial figure of II, but the same figure of V only appeared once (or twice) at the same place in five experiments.

Experiments were also made with staining solutions to try to discover a dye which would colour one modification whilst leaving the other unchanged. A number of dye stuffs, viz., crystal violet, Nile blue A, Congo red, water blue, ponceau, were tried, but all of them decomposed in contact with the salt.

The main results of the research may be summarised as follows :—

(a) From the dilatometric and crystallographic work no definite information is forthcoming which affords any precise proof as to a difference in properties of the two tetragonal modifications of ammonium nitrate.

(b) The argument derived from the investigation of the thermal properties tells, so far as it goes, against the identity of the two tetragonal modifications, but it cannot be considered as decisive.

In conclusion, I desire to express my thanks to Professor Arthur Schuster for placing at my disposal the resources of the physical laboratory of the Manchester University.

On the Osmotic Pressure of Compressible Solutions of any Degree of Concentration. Part II.—Cases in which both Solvent and Solute are Volatile.

By ALFRED W. PORTER, B.Sc., Fellow of, and Assistant Professor in,
University of London, University College.

(Communicated by Professor F. T. Trouton, F.R.S. Received January 30,—
Read February 20, 1908.)

In a former paper (to be referred to here as Part I) which appeared in the 'Proceedings of the Royal Society,'* I found an exact relation between vapour-pressures and osmotic pressure in the usual case in which the solute may be taken as involatile. The case now to be considered is the more general one in which both solvent and solute are volatile. The concentration and temperature in the main part of the paper are taken as constant; and the only restriction upon them is that the solutions and solvent must be capable of existing in the liquid form. The notation employed is the same as in Part I, any additional symbols being specially defined when they occur.

1. I shall make use of the general theorem, proved in Part I, that when a solution is in osmotic equilibrium with the pure solvent, the vapour-pressure of the solution is equal to the vapour-pressure of the pure solvent, each measured for the actual hydrostatic pressure of the fluid to which it refers; that is, with the former notation :

$$\pi_p = \pi_{0p}. \quad (1)$$

This was shown to be true whether the solute is volatile or not.

* A, vol. 79, 1907, pp. 519, *et seq.*

2. I shall utilise the formula giving the dependence of the vapour-pressure of the pure solvent upon hydrostatic pressure, viz. :—

$$\int_{p_0'}^{p_0} u dp = \int_{\pi_0 p_0'}^{\pi_0 p_0} v dp,$$

or, inserting the equality (1),

$$\int_{p_0'}^{p_0} u dp = \int_{\pi_0 p_0'}^{\pi_0 p_0} v dp. \quad (2)$$

The upper limits, which may be any corresponding values, shall be taken as

$$p_0 = \pi_{00} \quad \text{and} \quad \pi_{0 p_0} = \pi_{00}.$$

3. Let now an isothermal cycle of operations be performed upon a large (practically infinite) mass of solution at a pressure p in osmotic equilibrium with the solvent under a pressure p_0 . The sum of the external works done in the various stages of the cycle will be equated to zero. Let the solution

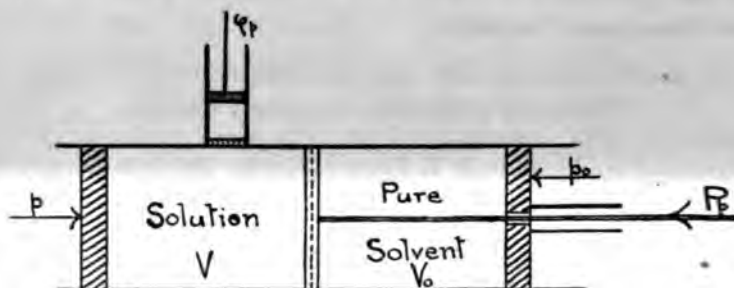


FIG. 1.

contain c grammes of solute to each gramme of solvent, the solute being defined as the constituent to which the membrane is impermeable. (In other respects it would, of course, be a matter of indifference as to which was considered to be solvent and which solute.)

Stage (a).—Force 1 gramme of the solvent out of the solution osmotically, letting the vapour of c grammes of the solute simultaneously escape into the lateral cylinder through a membrane semi-permeable alone to the vapour of the solute which is at a pressure ϕ_p . The work done upon the system in this two-fold change is

$$(1+c) P_p \sigma_p - p_0 (u_{p_0} - (1+c) \sigma_p) - \phi_p c w_p,$$

where w_p is the specific volume of the solute-vapour when in equilibrium with the solution under a hydrostatic pressure p , σ is the specific volume of the solution, and the other quantities have their previous meanings.

Stage (b).—Increase the pressure of the vapour thus formed to $\phi_{p'}$, simultaneously increasing the hydrostatic pressures of the solution and the solvent to the corresponding equilibrium values p' and p_0' respectively. The work done upon the system in this stage is

$$-c \int_{\phi_p}^{\phi_{p'}} \phi dw - \int_p^{p'} p d(V - (1+c)\sigma) - \int_{p_0}^{p_0'} p_0 d(V_0 + u_{p_0}),$$

where V and V_0 are the original volumes of the solution and the solvent.

Stage (c).—Restore the gramme of the solvent osmotically to the solution and simultaneously force in the c grammes of the solute-vapour from the lateral cylinder. The corresponding work is

$$-(1+c)P_{p'}\sigma_{p'} + p_0'(u_{p_0'} - (1+c)\sigma_{p'}) + c\phi_{p'}w_{p'}.$$

Stage (d).—Compress both the solution and the solvent to their original volumes and pressures. The work done is

$$-\int_{p'}^p p dV - \int_{p_0'}^{p_0} p_0 dV_0.$$

Each of these stages is reversible and isothermal, and the total work done must thence be zero. The sum, after integration by parts and simplification, is

$$(1+c) \int_{p'}^p \sigma dp = \int_{p_0'}^{p_0} u dp + c \int_{\phi_{p'}}^{\phi_p} w dp. \quad (3)$$

Now, the lower limits may be any equilibrium values, and we shall take them to be

$$p' = (\pi + \phi)_{(\pi + \phi)}, \quad \phi_{p'} = \phi_{\pi + \phi}.$$

These values of p' and $\phi_{p'}$ are respectively the pressure of the solution when in contact with the vapours of its constituents alone, and the corresponding pressure of the vapour of the solute.

4. Add together formulæ (2) and (3);

$$(1+c) \int_{(\pi + \phi)_{(\pi + \phi)}}^p \sigma dp + \int_{p_0'}^{\pi_{\infty}} u dp = \int_{p_0'}^{p_0} u dp + \int_{\pi_{p'}}^{\pi_{\infty}} v dp + c \int_{\phi_{(\pi + \phi)}}^{\phi_p} w dp;$$

or, since

$$\pi_{p'} = \pi_{(\pi + \phi)},$$

$$(1+c) \int_{(\pi + \phi)_{(\pi + \phi)}}^p \sigma dp = c \int_{\phi_{(\pi + \phi)}}^{\phi_p} w dp + \int_{\pi_{\infty}}^{p_0} u dp + \int_{\pi_{(\pi + \phi)}}^{\pi_{\infty}} v dp. \quad (4)$$

This is the formula desired; the osmotic pressure is $P_p = p - p_0$.

The connection between this formula and the more restricted one previously given is not immediately obvious. By considering a cycle in which, as in

Part I, 1 gramme of the solvent is allowed to escape through the osmotic membrane, and the c grammes of the solute are allowed to remain in the solution (which must be considered to have a practically infinite volume), the remainder of the cycle being conducted as above, I obtain the alternative expression

$$\int_{(\pi+\phi)(\pi+\phi)}^p sdp = \int_{\pi_0}^{p_0} udp + \int_{\pi(\pi+\phi)}^{\pi_0} vdp, \quad (4')$$

where s denotes the *shrinkage*, that is, the reduction of the practically infinite volume of the solution when 1 gramme of the solvent escapes; *i.e.*, $\left(\frac{\partial V}{\partial m_1}\right)_{m_2}$, where m_1 and m_2 denote the masses of the solvent and solute.

Comparing these two results, we see that

$$\int_{(\pi+\phi)(\pi+\phi)}^p sdp = (1+c) \int_{(\pi+\phi)(\pi+\phi)}^p \sigma dp - C \int_{\phi(\pi+\phi)}^{\phi_p} w dp.$$

This is an interesting connection between the shrinkage and the specific volume of the solution. Differentiating with respect to p , we obtain the equation

$$s_p = (1+c) \sigma_p - cw_{\phi_p} \frac{\partial \phi_p}{\partial p}. \quad (5)$$

The meaning of this equation will be examined in Section 6.

5. The above results have been obtained by making $\Sigma \int p dv$ round a reversible isothermal cycle equal to zero. But round such a cycle it is equally true that $\Sigma \int v dp$ is zero. The separate terms in this summation can be written down at once for the same cycle that has been considered. The result is the general equation (4) *without any further reduction*.

6. The mode of variation of vapour-pressure with the hydrostatic pressure to which the liquid is subjected can be determined by a slight modification of the method in Part I. The sole change required is that the liquid in the cylinder be enclosed by two pistons, the inner one of which is permeable to the vapour of the solvent, but impermeable to the vapour of the solute; the second piston must be impermeable to both. If the inner piston is maintained permanently in contact with the surface of the solution, none of the solute evaporates. The changes that proceed in the cycle considered are, therefore, precisely the same as for the case of an involatile solute, and the equation for the change of the vapour-pressure of the solvent with hydrostatic pressure comes out the same as before. Since each constituent may in turn be considered as the sole volatile one, a similar equation applies to each.

Hence we obtain

$$\partial\pi_p/\partial p = s_p/v_{\pi_p},$$

as before, and similar equations for the vapour-pressure of each of the other constituents present.

In each case $s_p = \partial V/\partial m$, where V is the total volume of the solution and m is the mass of the particular constituent to which s_p refers.

Examining equation (5) in the light of these results, we see that since $s_p = \left(\frac{\partial V}{\partial m_1}\right)_{m_2}$, where m_1 = mass of *solvent* present in the volume V ; and

$\omega_{\phi_p} \frac{\partial \phi_p}{\partial p} = \left(\frac{\partial V}{\partial m_2}\right)_{m_1}$, where m_2 is the mass of the solute, the equation becomes

$$\left(\frac{\partial V}{\partial m_1}\right)_{m_2} + c \left(\frac{\partial V}{\partial m_2}\right)_{m_1} = (1+c) \sigma_p = V, \quad (6)$$

and this is mathematically equivalent to the statement that σ_p is a function of c , that is of m_2/m_1 : a statement which of course is true.

7. The equation (4) is easily extended to the case where there are any number of volatile solutes present. It becomes

$$(1 + \Sigma(c)) \int_{[\pi + \Sigma(\phi)]}^p \sigma dp = \Sigma c \int_{\phi + \Sigma(\phi)}^{\phi_p} w dp + \int_{\pi_{\infty}}^{\pi_0} u dp + \int_{\pi_{\pi + \Sigma(\phi)}}^{\pi_{\infty}} v dp,$$

where the terms referring to the solvent are kept separate from the rest, because, owing to the special character of the osmotic membrane, the solvent is on a different footing from the other constituents.

When the solution is under the hydrostatic pressure of the vapours of its constituents alone, this equation reduces to the exceedingly simple one,

$$\int_{\pi_{\infty}}^{\pi_0} u dp + \int_{\pi_{\pi + \Sigma(\phi)}}^{\pi_{\infty}} v dp = 0.$$

This can be represented (as in Part I) on the indicator diagram of the pure solvent.

8. To find the variation of osmotic pressure with hydrostatic pressure, differentiate (4) with regard to p :

$$(1+c) \sigma_p = c w_{\phi_p} \frac{\partial \phi_p}{\partial p} + u_{\pi_0} \frac{\partial \pi_0}{\partial p} = c w \frac{\partial \phi_p}{\partial p} + u_{\pi_0} \left(1 - \frac{\partial P_p}{\partial p}\right).$$

By (5) this is equivalent to

$$s_p = u_{\pi_0} \left(1 - \frac{\partial P_p}{\partial p}\right).$$

Hence the variation of the osmotic pressure with the hydrostatic pressure of the solution is given by the same equation as for the case where the solute is involatile.

9. The theorem that the vapour-pressure of the pure solvent increases with the hydrostatic pressure can be obtained in a very simple way as follows :—

Let a vertical tube containing the solvent be enclosed in a closed chamber in a gravitational field, and let equilibrium be set up. Let now membranes permeable to the vapour alone be inserted in the side of the tube at a distance apart dh . Let p_0 be the hydrostatic pressure in the liquid at any point, and π_{0p_0} that in the vapour. Then u_{p_0} being the specific volume of the liquid, and $v_{\pi_{0p_0}}$ that of the vapour at the corresponding pressures, we have

$$dp_0 = -g \frac{dh}{u_{p_0}}, \quad d\pi_{0p_0} = -g \frac{dh}{v_{\pi_{0p_0}}},$$

whence

$$\frac{\partial \pi_{0p_0}}{\partial p_0} = \frac{u_{p_0}}{v_{\pi_{0p_0}}}.$$

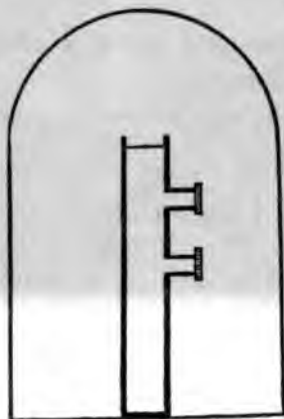


FIG. 2.

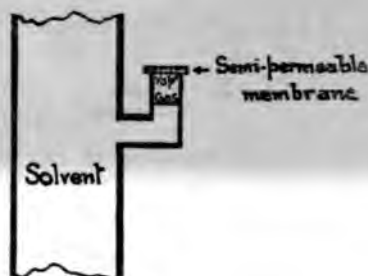


FIG. 3.

The semi-permeable membranes may be in direct contact with the liquid, or they may be separated from it by a space containing the vapour and an indifferent gas (see fig. 3).

This method is not applicable to the case of the vapour of a solution, because the concentration of the solution changes with the height. In this case,

$$\frac{dp}{dh} = -g\rho_p, \quad \frac{d\pi_p}{dh} = -\frac{g}{v_{\pi_p}}, \quad \frac{d\pi_p}{dh} = \left(\frac{\partial \pi_p}{\partial c}\right)_p \frac{dc}{dh} + \left(\frac{\partial \pi_p}{\partial p}\right)_c \frac{dp}{dh},$$

whence

$$\left(\frac{\partial \pi_p}{\partial c}\right)_p \frac{dc}{dh} = -g \left(\frac{1}{v_{\pi_p}} - \frac{\partial \pi_p}{\partial p} \rho_p \right).$$

Making use of the values obtained previously in this paper, some interesting results can, however, be obtained. We have

$$\frac{\partial \pi_p}{\partial p} = \frac{s_p}{v_{\pi_p}}, \quad \rho_p = \frac{1}{\sigma_p},$$

and writing

$$(\partial V / dm_2)_{m_1} \equiv s_p',$$

$$\left(\frac{\partial \pi_p}{\partial c} \right)_p \frac{dc}{dh} = - \frac{g}{v_{\pi_p}} \left(1 - \frac{s_p}{\sigma_p} \right).$$

By means of equation (4) this may be written

$$\left(\frac{\partial \pi_p}{\partial c} \right)_p \frac{dc}{dh} = - \frac{gc}{v_{\pi_p}} \frac{s_p' - s_p}{s_p + cs_p'}.$$

In the same way, if the semi-permeable membranes are permeable only to the vapour of the solute, we have

$$\left(\frac{\partial \phi_p}{\partial c} \right)_p \cdot \frac{dc}{dh} = - \frac{g}{w_{\phi_p}} \left(1 - \frac{s_p'}{\sigma_p} \right) = - \frac{g}{w_{\pi_p}} \frac{s_p - s_p'}{s_p + cs_p'}.$$

It will be seen from these equations that if $s_p' = s_p$, then either

$$\left(\frac{\partial \pi_p}{\partial c} \right)_p = 0, \quad \text{or} \quad \frac{dc}{dh} = 0.$$

Now comparison with equation (6) shows that when $s_p' = s_p$ each is equal to σ_p . This can only occur when the densities of the two constituents are nearly alike.

In all such thermodynamic equations $\left(\frac{\partial \pi_p}{\partial c} \right)_p$ and $\frac{dc}{dh}$ appear together. It would seem to be impossible to separate them.

Summary of Results.

1. An exact equation is obtained for the connection between osmotic pressure and the vapour-pressures of a solution and a solvent for compressible solutions of any degree of concentration.
2. The mode of variation of the vapour-pressure of *each* solute with hydrostatic pressure is found. This is given for each by the same formula as if the other solutes were absent.
3. The result is extended to the case of any number of volatile constituents. When the hydrostatic pressure of the *solution* is that due alone to the vapours of its constituents the equation reduces to as simple a form as when the constituents are involatile.
4. The osmotic pressure is found to change with hydrostatic pressure according to the same formula as when the solute is involatile.
5. A very simple proof is given of the variation of the vapour-pressure of a pure liquid with hydrostatic pressure. This proof cannot be extended to the case of a solution owing to a space-variation of concentration being set up under the conditions of the proof.

Addendum.—Received February 20, 1908.

In a previous paper* I have given an exact formula for the increase of vapour-pressure of a liquid with the hydrostatic pressure to which the liquid is subjected. This variation actually occurs in several familiar phenomena which can, therefore, all be linked together under one head.

1. The first of these phenomena which I shall consider is that of the difference of vapour-pressure for a curved and that for a plane surface. Let π be the vapour-pressure at a plane surface of a simple liquid in contact with its own vapour alone, so that its hydrostatic pressure is also π ; let π' be the vapour-pressure of the same liquid when in the form of a drop of radius R , and let T be the surface-tension. Then the hydrostatic pressure of the liquid in the latter case is $\pi' + 2T/R$.

Now in the paper referred to I have shown that

$$d\pi_p/dp = u_p/v_{\pi_p},$$

where u_p is the specific volume of the liquid,

π_p „ vapour-pressure,

and v_{π_p} „ specific volume of the vapour at the pressure π_p .

Hence, treating the change as small, we have, approximately,

$$\frac{\pi' - \pi}{\pi' - \pi + 2T/R} = \frac{u_\pi}{v_\pi}, \quad \text{or} \quad \pi' - \pi = \frac{2T}{R} \cdot \frac{u_\pi}{v_\pi - u_\pi}.$$

This is Kelvin's formula, expressed, however, in terms of specific volumes instead of in terms of densities as usual.

It is clear that if the hydrostatic pressure at the flat surface were increased to an equal amount by superposing an atmosphere of an independent gas, the vapour-pressure at the curved surface would not be different from that at the plane surface.

2. The next phenomenon is that of the change of vapour-pressure due to imparting an electric charge of surface density σ . The usual formula is obtainable by substituting $-2\pi\sigma^2$ for $2T/R$. It follows, therefore, that the change of vapour-pressure in this case is also directly due to the change in hydrostatic pressure: it is unnecessary to invoke any recondite effect of the electrification upon the surface.

3. The difference in the vapour-pressure of a solution from that of the pure solvent, when both are at the same hydrostatic pressure, can also be attributed to the fact that the partial pressure of the solvent in the solution is then less than the total pressure. In making this statement, I regard the hydrostatic pressure p of the solution as made up of: (a) a partial pressure,

* 'Roy. Soc. Proc.,' A, vol. 79, 1907, p. 525.

equal to the osmotic pressure P due to the salt; (b) a partial pressure p_0 due to the solvent, so that $p - p_0 = P$. I must recall the fact that I have proved* that when a solution is in equilibrium with the pure solvent, the vapour-pressures of both are the same. That is to say, the vapour-pressure of a solution at a hydrostatic pressure p is the same as the vapour-pressure of the solvent under a hydrostatic pressure p_0 where these pressures differ by the amount P . So that, provided the partial pressure of the solvent is the same, the vapour-pressure is the same whether it is in a solution or not.

Conclusion.

I have thus considered several cases in which the vapour-pressure is changed, and found that in each case it is only necessary to know the partial pressure of the pure solvent whose vapour we refer to in order to calculate what the change in the vapour-pressure amounts to. The same method might presumably be applied to other cases also, such as magnetisation, etc. In this addendum the approximate formulæ only have been given, in order that comparison may be made at once with familiar formulæ. The exact forms can easily be written down when required.

* *Loc. cit.*, p. 526.

On Vapour-pressure and Osmotic Pressure of Strong Solutions.

By H. L. CALLENDAR, F.R.S., Professor of Physics at the Imperial College of Science and Technology.

(Received March 10,—Read March 19, 1908.)

1. The relations between vapour-pressure, osmotic pressure, and concentration of solutions are of great interest, and have been the subject of recent communications by Lord Berkeley and Hartley, by Spens, and by Porter. I propose in the present paper to develop a theory of solutions, based on a simple relation between the vapour-pressure and the concentration, which appears to give a very fair account of the phenomena observed in the case of strong solutions, and is at the same time a natural extension of the present theory as applied to dilute solutions. Before discussing the theory itself, I propose to give fresh proofs of some of the more important relations already accepted, for the sake of indicating clearly the order of approximation attempted, and of illustrating methods of proof which I have employed in teaching for many years, but which do not appear to be generally known.

Relation between Vapour-pressure and Hydrostatic Pressure.

2. By considering the isothermal equilibrium of a liquid and its vapour in a capillary tube of radius r , Lord Kelvin* deduced the well-known relation between the vapour-pressure p at the curved surface and the normal vapour-pressure p_0 at a plane surface, in terms of the surface tension T , and the densities of the liquid and vapour ρ and σ ,

$$p - p_0 = 2T\sigma/r(\rho - \sigma), \quad (1)$$

where r is positive if the surface is convex. The effect was regarded by Lord Kelvin as being due to curvature, but Poynting† showed that it might be regarded simply as an effect of hydrostatic pressure, and explained the equilibrium of ice and water under pressure on this basis. Since the pressure P inside a spherical drop of radius r exceeds the vapour-pressure p outside it by $2T/r$, substituting $(P - p)$ for $2T/r$ we obtain,

$$p - p_0 = (P - p)\sigma/(\rho - \sigma) = (P - p_0)\sigma/\rho, \quad (2)$$

which is equivalent to the expression given by Poynting. Since the relation

* 'Phil. Mag.,' [4], vol. 42, p. 448, 1871.

† 'Phil. Mag.,' [12], p. 40, 1881.

applies only to small differences of pressure in this form, it is more convenient to write it in the differential notation

$$v dp = V dP, \quad (3)$$

which is perfectly general and accurate if V and v are the specific volumes of the liquid and vapour at the pressures P and p respectively. By integrating equation (3) between corresponding limits of P and p , the variation of vapour-pressure with pressure may be obtained with considerable accuracy over wide ranges of pressure and temperature. The principal source of uncertainty is the compressibility of the liquid. If we put $V = V_0(1 - \alpha P)$, assuming the compressibility α to be constant, and if we take $v = R'\theta/p - c + b^*$ (where $c - b$ represents the defect of volume of the vapour from the ideal volume $R\theta/p$, and is to a first approximation a function of the temperature only), we obtain

$$R'\theta \log_e (p/p_0) = (c - b)(p - p_0) + V_0(P - P_0) - \frac{1}{2}\alpha V_0(P^2 - P_0^2), \quad (4)$$

where P , p , and P_0 , p_0 , are corresponding limits of P and p . According to this equation it would require a pressure of about 2000 atmospheres only to increase the vapour-pressure of water fourfold at 27°C . The approximate equation (2), which is often applied to such calculations, would give upwards of 4600 atmospheres. The term $(c - b)(p - p_0)$ is negligible at this temperature, as p is so small, but it amounts to about 17 per cent. at 200°C , if $p/p_0 = 4$. It has the effect of considerably reducing the pressure required when p is large.

Vapour-sieve Method.

3. It is easier to form a mental picture of the variation of vapour-pressure with hydrostatic pressure, if we imagine the liquid contained in a long vertical tube perforated with very fine holes. If the holes are fine enough and are not wetted by the liquid, the liquid cannot escape, but the vapour has free passage. If such a tube is surrounded by vapour in an isothermal enclosure, the liquid must be in equilibrium with its vapour at all points, which leads immediately to equation (3). If the holes are wetted by the liquid the same arrangement will apply for negative values of P . Poynting† deduces that the pressure of the vapour molecules in the interior of the liquid at any point of such a tube must be everywhere *proportional* to the pressure of the vapour immediately outside the tube. There is reason for believing that the vapour-pressure in the liquid is not merely proportional to that outside, but is *equal* to it, in other words that it is everywhere the same as if the liquid were

* Callendar, 'Roy. Soc. Proc.' vol. 67, p. 270, 1900. R' is the gas-constant, $R = 1.98$ calories, divided by the molecular weight m of the vapour.

† *Loc. cit.*

absent. I have shown* that such an assumption appears to account satisfactorily for the variation of the specific heat in the case of water.

The same reasoning precisely applies if the vapour-sieve tube contains any solution in place of a pure liquid. Equilibrium will be rapidly established by condensation or evaporation of the vapour until condition (3) is satisfied. A column of pure solvent in equilibrium with the same vapour column must be in equilibrium with the solution at corresponding heights. If the holes in the vapour-sieve are fine enough to permit passage only to the vapour molecules, we may imagine the solution column surrounded by the solvent column without disturbing the equilibrium. The difference of hydrostatic pressure between the columns of solution and solvent at any height is the osmotic pressure corresponding to the concentration and hydrostatic pressure of the solution at the point considered. In other words, we may regard a semi-permeable membrane, such as is usually postulated in considering osmotic pressure, as being in reality a vapour-sieve, permeable only to the vapour. Such an assumption does not appear to be inconsistent with any of the well-established facts regarding osmotic pressure, and gives a somewhat simpler physical conception of the phenomena of osmosis.

Application of the Vapour-sieve Piston.

4. Without assuming that a vapour-sieve might be made to act as a semi-permeable membrane in osmotic experiments between solution and solvent, it is easy to show by the application of a vapour-sieve piston that the vapour-pressures of solution and solvent are the same (under any hydrostatic pressures) when they are in osmotic equilibrium through a semi-permeable membrane. Suppose that the solution and solvent are in equilibrium, as indicated in fig. 1, on either side of a semi-permeable membrane B under pressures P'' and P' applied by means of vapour-sieve pistons A and C. The pressure-difference $P'' - P'$ is the osmotic pressure P_o . If the arrangement is contained in an isothermal enclosure, through which the vapour has free circulation, the vapour-pressure p'' of the solution under pressure P'' must be equal to the vapour-pressure p' of the solvent under pressure P' . Otherwise a continuous supply of work might be obtained by utilising the pressure-difference of the vapour. By similar reasoning we may assert generally that any two solutions in equilibrium through any kind of membrane or capillary surface must have the same vapour-pressures in respect of each of their constituents which are capable of diffusing through the surface of separation. This has for a long time been

* 'Phil. Trans.,' A, 1902, p. 147.

generally admitted, but the vapour-sieve piston supplies what is perhaps the simplest proof based on known physical properties.

We have seen that equation (3) must apply accurately to the equilibrium between a vertical column of solution and vapour under the action of gravity, but there is one respect in which the equilibrium of such a solution differs from that of the pure solvent. The concentration of the solution is independently variable, and must vary in such a manner as to make equation (3) hold. The variation of vapour-pressure with height in such a column of solution is not necessarily that due to variation of pressure alone. This has been recognised by Spens and Porter, who have deduced the variation with pressure independently of concentration, by the method of an isothermal cycle. The cycles which they employ appear, however, to be unnecessarily complicated. Porter applies pressure by means of an inert gas, which is assumed not to dissolve in the liquid or alter its vapour-pressure, and which adds unnecessary terms to the equation, besides requiring the

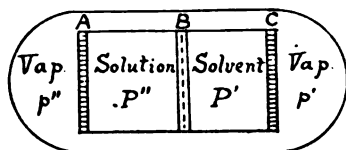


FIG. 1.—Equality of Vapour-pressure in Osmotic Equilibrium.

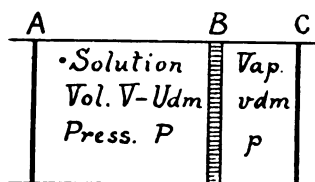


FIG. 2.—Change of Vapour-pressure of a Solution with Hydrostatic Pressure.

application of an additional piston permeable to the vapour but not to the gas. The result may be more simply and directly deduced by the aid of a vapour-sieve alone.

Imagine unit mass of solution of volume V , confined in a cylinder ABC between a fixed vapour-sieve B, and a solid piston A, by which pressure P is applied. The vapour, at pressure p , corresponding to P , is confined by a solid piston C, which we will suppose at first to be in contact with B, so that the volume of the vapour is initially zero. The cycle is as follows:—

(1) Keeping the pressures constant, evaporate a small mass dm of solvent. The work done by the piston C is $pv \, dm$. The work done on the piston A is $PU \, dm$, where U is the rate of diminution of volume of the solution at a pressure P per unit mass of solvent abstracted. The volume of solution remaining is now $V - U \, dm$. The state of the system at this stage is that represented in fig. 2.

(2) Increase the pressure on the solution to P' , by means of the piston A, at the same time moving the piston C, so as to keep the vapour in equilibrium with the solution without condensation. Suppose the pressure of the

vapour is increased to p' . The work done on the system is given by the expression,

$$-\int_P^{P'} P d(V - U dm) - \int_p^{p'} p dv dm.$$

(3) Keeping the pressures constant at P' and p' , condense the mass dm of vapour by moving piston C into contact with B, at the same time moving piston A outwards through a space $U' dm$, where U' is the value of U corresponding to pressure P' . The work done on the system is

$$-P'U' dm + p'v' dm.$$

(4) Release the pressure on the solution to its original value P , restoring the original volume V . The work done on the system is $+\int_P^{P'} P dV$.

Collecting the terms, and observing that $p'v' - pv = \int_p^{p'} p dv + \int_p^{p'} v dp$, we obtain finally,

$$\int_P^{P'} U dP = \int_p^{p'} v dp, \quad \text{or} \quad U dP = v dp, \quad (5)$$

which expresses the variation of vapour-pressure of a solution with pressure alone, assuming the temperature and concentration constant.

Variation of Concentration in a Vertical Column.

5. It appears from this result that the concentration of a vertical column of solution will not remain uniform when in equilibrium with the vapour at all heights, unless $U = V$ for the solution. If the whole length of the column is in contact with the vapour through a vapour-sieve envelope, the attainment of equilibrium with the vapour by condensation and evaporation would be comparatively rapid if the temperature is maintained uniform. If the solution were contained in an impervious tube, the same final result would be produced by diffusion of the vapour through the solution, but the attainment of equilibrium would be very slow.

Since the whole change of vapour-pressure in such a column in the equilibrium state is given by $v dp = V dP$, and the partial change dp' due to pressure is given by $v dp' = U dP$, the change dp'' due to change of concentration is given by $v dp'' = (V - U) dP$. If $V - U$ is negative, which is generally the case, the increase of vapour-pressure downwards in such a column will be less than that due to pressure alone, and the concentration will increase with depth. The values of $V - U$ for any solution are readily deduced from a table of densities or specific volumes V for any concentration C in grammes of solute per gramme of solution, by the relation

$$V - U = C (dV/dC), \quad (6)$$

which shows that $V - U$ is negative when the density increases with concentration.

Variation of Osmotic Pressure with Hydrostatic Pressure.

6. Since the osmotic pressure is the difference of the hydrostatic pressures P' and P'' of the solution and solvent when their vapour-pressures are equal, the variation of osmotic pressure with hydrostatic pressure is readily deduced from equation (5). If W is the specific volume of the pure solvent, we must have for equilibrium, $W dP' = U dP''$, since each is equal to $v dp'$. The corresponding change of osmotic pressure dP_0 is equal to the difference $dP'' - dP'$, whence,

$$dP_0/dP' = (W - U)/U, \text{ or } dP_0/dP'' = (W - U)/W. \quad (7)$$

If $U = W$ there is no change in the osmotic pressure with hydrostatic pressure. This is equivalent to the assumption made by Lord Berkeley and Mr. Hartley* that the osmotic pressure varies with concentration only, which appears from their experiments to be approximately true for some solutions.

The relation between the equilibrium pressures P' and P'' for solution and solvent corresponding to the same value p_0 of the vapour-pressure is immediately obtained by integrating formula (5) between corresponding limits for solution and solvent. We have evidently,

$$\int_{p''}^{p'} U dP'' = \int_{p''}^{p_0} v dp, \text{ and } \int_{p'}^{p''} W dP' = \int_{p'}^{p_0} v dp,$$

$$\text{whence} \quad \int_{p''}^{p'} U dP'' - \int_{p'}^{p''} W dP' = \int_{p''}^{p'} v dp, \quad (8)$$

where p', p'' are the vapour-pressures of solution and solvent, each under the pressure of its vapour only. This agrees precisely with the result obtained by Porter, but it seems better to deduce it from (5) in place of employing a special cycle.

The osmotic pressure may readily be deduced from the vapour-pressures p' and p'' , for any value of P' or P'' if the value of U is known. The most uncertain element in the calculation is the variation of U with pressure. If P_0' is the value of the osmotic pressure $P'' - P'$ when the solvent is under its own vapour-pressure p' only, or when $P' = p' = p_0$, the term containing W vanishes, and the limit of integration P'' is $P_0' + p'$. Similarly, if P_0'' is the osmotic pressure when the solution is under its own vapour-pressure p'' only, or when $P'' = p''$ and $P' = p'' - P_0''$, the term containing

* 'Roy. Soc. Proc.,' A, vol. 77, p. 156, 1906.

U vanishes. The limits of the integral $v dp$ are the same in both cases, and we obtain, assuming $v = R'\theta/p - c + b$,

$$(P_0' + p' - p'') U_0 = R'\theta \log (p'/p'') - (c-b)(p' - p'') = (P_0'' + p' - p'') W_0, \quad (9)$$

where U_0 , W_0 , are the mean values of U and W taken with respect to pressure between the corresponding limits of integration.

The term containing $(c-b)$ is retained, though unimportant at ordinary temperatures, because $(c-b)$ is about 75 times as large as W for water at 0°C. ,* and because it becomes important in comparison with $R\theta$ when p is large.

For most experimental purposes the small terms involving the factor $(p' - p'')$ may be neglected. We then have, approximately,

$$P_0' U_0 = R'\theta \log (p'/p'') = P_0'' W_0. \quad (10)$$

The values of P_0'' are the same for solutions having the same vapour-pressure p'' : or the values of the vapour-pressure will be very nearly the same for isotonic solutions tested under atmospheric pressure. But P_0'' cannot be directly measured by balancing against the pure solvent, as the corresponding value of the pressure on the solvent is large and negative, being approximately equal to $-P_0''$. The osmotic pressure measured by direct experiment, with the solvent under atmospheric pressure, is approximately equal to P_0' , and is correctly related to the vapour-pressure p'' of the same solution by equation (10), as was proved approximately by Spens, but more accurately by Porter.

For an actual vertical column of solution in equilibrium, equation (3) applies accurately, with V the specific volume of the solution in place of U . This gives the approximate equation usually quoted, namely,

$$P_0 V_0 = R'\theta \log (p'/p''), \quad (11)$$

where V_0 is the mean specific volume of the solution column, P_0 is the osmotic pressure *at the bottom* of the column, and p'' is the vapour-pressure at the top, where the concentration is generally different. Lord Berkeley and Mr. Hartley, in comparing their observations of vapour-pressure and osmotic pressure for the same solutions, found that the values of the osmotic pressure calculated from the vapour-pressure by equation (11) were much larger than those directly measured for the same solutions, and rightly attributed the discrepancy to variation of concentration in the imaginary

* Porter and Spens retain the term $U(p' - p'')$, but neglect the much larger term $(c-b)(p' - p'')$.

vertical column by which equation (11) is deduced. They therefore deduced the expression,

$$P_0''W_0 = R'\theta \log(p'/p''), \quad (12)$$

which correctly represents the relation between the osmotic pressure P_0'' and the vapour-pressure p'' of the solution *at the top* of such a column. In applying this equation to the conditions of their experiments, they made the assumption that the osmotic pressure could vary only with concentration, and that the value of P_0'' calculated from p'' by equation (12) for the osmotic pressure at the top of the column (where the solvent is under negative pressure) would be the same as the osmotic pressure directly measured for a solution of the same concentration with the solvent under atmospheric pressure. The approximate agreement of their observations with equation (12) would appear to imply, as Spens pointed out, that U is nearly equal to W for the solutions they employed. Strictly speaking, the value of P_0'' given by equation (10) or (12) is not equal to that of P_0' in equation (10), even if $U = W$ when solution and solvent are under the same pressure, because the mean values U_0 and W_0 are taken for positive and negative pressures respectively. The difference, however, would amount to less than 1 per cent. for the largest pressures measured by Lord Berkeley and Mr. Hartley.

Example of Variation of Concentration in a Vertical Column.

7. The variation of concentration in a vertical column of solution under gravity can be determined if the density and osmotic pressure are known as functions of the concentration. The osmotic pressure P_0 at the bottom of such a column given by equation (11) exceeds the value of P_0 , given by equation (10) for a solution having a composition corresponding to the normal vapour-pressure p'' , in the proportion of U_0 to V_0 . For strong solutions, the value of V_0 may be determined readily by successive approximation. But if the difference is small, and if the concentration C is defined as in equation (6), we have the approximate relation,

$$dC/C = -P(dV/dP)/V, \quad (13)$$

where dV is the change of V corresponding to the difference of osmotic pressures $dP = P_0 - P_0'$, and C , P , and V , are the mean values of the concentration, osmotic pressure, and specific volume for the column.

It may be interesting to give, as an example, the variation of concentration in a vertical column for the solutions examined by Lord Berkeley and Mr. Hartley, for which the requisite data are available. They give the concentration in grammes of sugar per litre of solution at 0° C. If the

concentration measured in this way is denoted by C' , while C denotes, as before, the concentration in grammes per gramme of solution, we have $C' = 1000 C/V$. The values of U and V for the solutions at 0° C. are calculated from Landolt and Bornstein's tables of the densities of cane-sugar solutions at 0° C., in which the concentration is expressed in grammes of sugar per 100 grammes of solution.

Table I.—Variation of Concentration in a Vertical Column of Solution of Cane-sugar at 0° C.

| C' | U | V | P_0' | P_0 | V_0 | C_0' | $C_0' - C'$ | Per cent. |
|------|-------|-------|--------|-------|-------|--------|-------------|-----------|
| 760 | 0.986 | 0.775 | 134.0 | 172.0 | 0.767 | 900 | 140 | 18.4 |
| 660 | 0.990 | 0.795 | 101.0 | 126.0 | 0.787 | 741 | 81 | 12.3 |
| 540 | 0.993 | 0.825 | 67.5 | 82.0 | 0.817 | 600 | 60 | 11.1 |
| 420 | 0.996 | 0.858 | 44.0 | 51.5 | 0.852 | 460 | 40 | 9.5 |
| 300 | 0.998 | 0.895 | 26.8 | 30.2 | 0.897 | 325 | 25 | 8.3 |
| 180 | 0.999 | 0.932 | 14.0 | 15.1 | 0.930 | 193 | 13 | 7.3 |

The first four columns contain the data for the solutions employed, and correspond to the concentration at the top of the imaginary vertical column. P_0 and C_0' are the osmotic pressure and concentration at the bottom of the column. V_0 is the mean specific volume, which is seen to differ little from that at the top. The variation of concentration is considerable, and illustrates the order of error involved in applying the usual formula (12) to the case of strong solutions. The numbers in the last column appear to indicate a systematic error in the experimental numbers for strong solutions. They would be more regular if the theoretical expression given below for the osmotic pressure were employed in the calculation.

The Cellular Osmotic Column.

8. A case of special interest, as corresponding more closely with the kind of osmotic column which actually occurs in nature, is the cellular osmotic column. If a series of minute osmotic cells with flexible walls are disposed in a vertical column supported by fibrous material, and surrounded by an atmosphere of vapour, the hydrostatic pressure will be nearly uniform throughout the column, and equal to the vapour-pressure. Such a column will be in equilibrium when the concentration at any height is such that the vapour-pressure of the solution is equal to that in a column of vapour at the same height. Supposing that the vapour-pressure at the base is equal to that of the pure solvent, the concentration will increase from zero upwards, and the osmotic pressure referred to pure solvent at any height is that given

by equation (10). The concentration at any height is the same as that at the top of a continuous column of solution of the same height, but the elevation of the solvent is obtained more economically, without any excessive pressure differences, and with less than half the quantity of dissolved substance.

Since the osmotic pressure at any height depends on U , and not on V as in a continuous vertical column, it would appear at first sight as though the action of gravity in changing the concentration were eliminated by the cellular arrangement. But this is not the case, because the concentration in each little cell must vary in the same way as in a vertical column. The effect of this is to make the elementary difference of osmotic pressure between the top of one cell and the bottom of the next greater in the proportion of U to V than it would be if the concentration were uniform in each cell. Since the direction of the change of concentration in each cell depends on the direction of gravity, it would appear that gravity must exert some directive action on the growth of the plant on this account. In a growing plant the conditions are seldom those of equilibrium or constant temperature, and many other factors are operative, but the consideration of the condition of equilibrium is important, because the rate of osmosis will be determined chiefly by the extent of the departure from the condition of equilibrium.

Method of the Osmotic Circuit.

9. A circuit consisting of different phases containing one component in common presents many points of analogy with an electric circuit. The analogy is particularly close between thermoelectric and osmotic circuits. The electromotive force round a circuit is measured by the work done in taking unit quantity of electricity round the circuit, and is zero in a thermoelectric circuit when there is no difference of temperature. Similarly, in an osmotic circuit in equilibrium at uniform temperature, the work done in taking unit mass of solvent round the circuit must be zero. Neglecting external forces, such as gravity, the work done is represented by the integral of $U dP$ taken round the circuit between limits corresponding to the transition points between the phases, where U is the increase of volume of the phase considered per unit mass of solvent added at a pressure P . The method of the osmotic circuit essentially corresponds to the more familiar method of the isothermal cycle, but it has the advantage that the limits of integration are obvious, and that the correct result can be written down in any case by mere inspection; whereas the method of the isothermal cycle is often very complicated and difficult to follow, as may be seen by reference to the

examples given by Spens and Porter. A number of unnecessary terms are introduced, and the greatest care is required to avoid making mistakes, of which a large number might be cited.

If we consider a vertical column of liquid or solid, in equilibrium with its vapour through a vapour-sieve envelope as in Section 2, taking the integral of $v dp$ round any circuit partly in the vapour and partly in the liquid or solid, we obtain immediately equation (3) and its corresponding integral. In the case of a pure liquid, the work done against gravity is negligible, because U is the same as V , the specific volume of the liquid, at all points. In the case of a solution, where U may differ from V , the work done against gravity in raising a mass of specific volume U through a solution of specific volume V , which is represented by the integral of $(V-U)dP$ per unit mass, must be added to the integral of UdP in the solution. This has the effect of replacing U by V in the equation, as already explained in Section 5, and takes account of the effect of gravity in altering the concentration. If this effect of gravity is neglected, and the solution assumed uniform, the method naturally gives the effect of pressure alone, as represented by equation (5).

Analogy with the Isothermal Cycle.

10. A closer correspondence between the circuit method and the method of the isothermal reversible cycle is obtained if we suppose the pressure-differences in the circuit utilised for the performance of external work by means of imaginary isothermal reversible motors or pumps. Let fig. 3

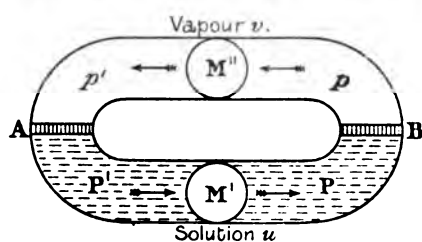


FIG. 3.—Osmotic Circuit, giving Variation of Vapour-pressure of Solution with Hydrostatic Pressure P .

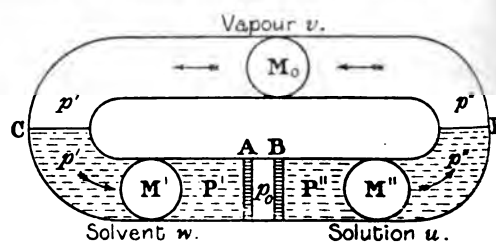


FIG. 4.—Osmotic Circuit for Solvent, Solution and Vapour.

represent such a circuit consisting of solution and vapour separated by vapour-sieve partitions A and B. Suppose isothermal reversible motors M' , M'' , included in the circuit, separating the solution into two parts under pressures P and P' , and the vapour into two parts under corresponding pressures p and p' . If the temperature is maintained uniform, the work done by the motor M' per unit mass of solvent passing through it must be

equal and opposite to that done by the motor M'' . No external work is done at other points of the circuit. The work done per unit mass passing through the motor M' is evidently

$$P'U' + \int_{P'}^P P dU - PU = \int_P^{P'} U dP. \quad (14)$$

Similarly the work done per unit mass of the vapour passing through the motor M'' in the direction indicated by the arrows is given by $\int_{P'}^P v dp$. The sum of these must be equal to zero, which corresponds with the result of the isothermal cycle represented by equation (5).

As an additional complication, we may introduce the solvent into the circuit (though this is really unnecessary, and does not prove anything new), as indicated in fig. 4, by supposing it separated from the solution by a semi-permeable membrane under pressures P' and P'' respectively, such that $P' - P''$ equals the osmotic pressure P_0 . An equivalent method is to employ a pair of vapour-sieve partitions A and B, separated by a space containing vapour at the common pressure p_0 . The motors M' , M'' serve to reduce the pressures of the solvent and solution respectively to equilibrium with their normal vapour-pressures p' , p'' . The vapour is separated into two parts at pressures p' and p'' by the motor M_0 . Equating to zero the sum of the external work done by the three motors, we have evidently,

$$\int_{P''}^{P'} U dP + \int_{P'}^{P''} v dp + \int_{P'}^{P''} W dP = 0. \quad (15)$$

This corresponds with the isothermal cycle worked out by Porter,* but the circuit method enables the whole process to be displayed graphically, and the physical interpretation of each term in the result is made immediately obvious.

Effect of Pressure on the Latent Heat of Vaporisation.

11. In an isothermal circuit or cycle the algebraic sum of the quantities of heat absorbed and liberated must also be equal to zero. Applied to the isothermal circuit of fig. 1, in which solvent and solution are in osmotic equilibrium under pressures P' and P'' , this condition leads to the result that the latent heat of vaporisation of the solution at A must be equal to the latent heat of condensation of the solvent at C, under the same vapour-pressure plus the heat Q_0 evolved on dilution at B.

$$L'' = L' + Q_0. \quad (16)$$

Applied to the osmotic circuit of fig. 3, the condition gives the rate of

* *Loc. cit.*

variation of the latent heat of vaporisation of a solution with change of pressure at constant temperature. The heat absorbed in vaporisation at A, plus the heat absorbed in the motor M'', equals the heat evolved in condensation at B, plus the heat evolved in the motor M'. Supposing for convenience that the difference of pressure is small, or that $P' - P = dP$, and $p' - p = dp$, the heat absorbed in the motor M'' is $-\theta dp (dv/d\theta)$, which is approximately equal to the work done $-v dp$, since $(dv/d\theta)$ is nearly equal to v/θ for the vapour. The heat absorbed in the motor M' is similarly equal to $-\theta dP (dU/d\theta)_P$. Since $v dp = U dP$, we have evidently the relation,

$$(dL/dP)_\theta = U - \theta (dU/d\theta)_P. \quad (17)$$

A precisely similar relation applies for the pure solvent, with the substitution of W , the specific volume of the pure solvent, in place of U . If we apply this relation to the case of water at 4°C ., at which temperature $(dW/d\theta) = 0$ under atmospheric pressure, we find the rate of increase of the latent heat per atmosphere (10^6) of pressure equal to 10^6 ergs, or a pressure of about 42 atmospheres would be required to increase the latent heat by 1 calorie. The change at other temperatures can be deduced from a knowledge of the coefficient of expansion.

Theory of Osmotic Pressure.

12. The several theories of osmotic pressure now current may be roughly classified under four heads: (1) The gas-pressure theory, according to which the osmotic pressure due to the molecules of the solute is the same as that which would be exerted by the same number of molecules of gas occupying the same volume at the same temperature. (2) The surface-tension theory, according to which the pressure developed is due to surface-action or difference of surface-tension. (3) The association, or hydrate theory, according to which the effects are due to residual chemical affinity between solvent and solute, resulting in the formation of hydrates or similar molecular complexes. (4) The vapour-pressure theory, according to which the osmotic pressure is simply the pressure required to produce equilibrium of vapour-pressure between the solvent and solution. It is probable that all the theories possess some elements of truth, and that they may be to some extent merely different aspects of the same phenomenon.

As an illustration of the deviation of the experimental results from the usually accepted theory, the observations of Lord Berkeley and Mr. Hantley on the osmotic pressures of strong solutions of cane-sugar and dextrose at 0°C . are plotted in the accompanying diagram, fig. 5. In their papers the results are tabulated and plotted in terms of concentration C' in grammes

of sugar *per litre of solution*, which has generally been adopted in dealing with osmotic pressure in consequence of Vau't Hoff's theory. It is more convenient, however, in dealing with osmotic pressures or depressions of the freezing-point in strong solutions, to plot the results in terms of concentration C'' expressed in grammes of solute per gramme of solvent, because for normal solutions such as cane-sugar the curves are more nearly straight, and the deviation of the observations from the theoretical curves can be

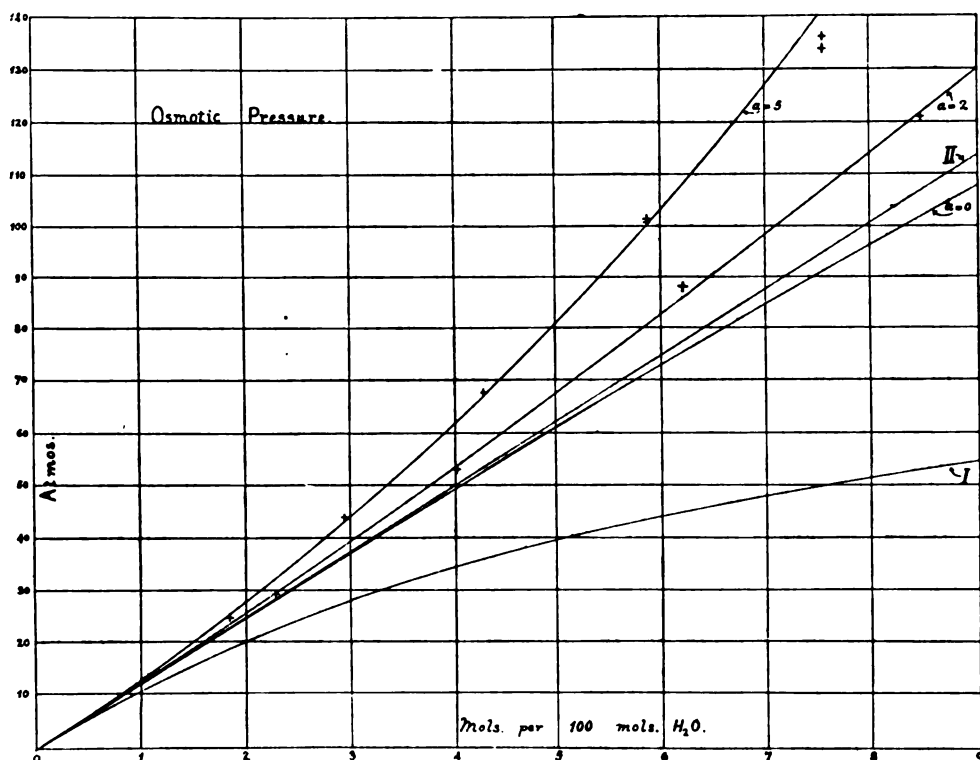


FIG. 5.—Osmotic Pressures of Solutions of Cane-sugar and Dextrose.

more readily estimated. In dealing with densities or specific volumes it is generally better to employ the percentage concentration 100 C (grammes of solute per 100 grammes of solution) in terms of which they are usually tabulated. The relation between the three modes of expressing the concentration is

$$C'V = C = C''/(1+C'').$$

In comparing solutions of different substances it is necessary to plot the results in terms of the ratio of the number of molecules n of the dissolved substance to the number of molecules N of the solvent in the solution,

because the relations involved are of a molecular nature. We have $n/N = mC''/M$, where m and M are the molecular weights of solvent and solute respectively. In plotting the observations in fig. 5, N is taken as equal to 100, and the values of the osmotic pressure are plotted against the number n of molecules of solute to 100 molecules of solvent. The molecular weight of water is taken as 18, and the corresponding values for cane-sugar and dextrose as 342 and 180 respectively, which are sufficiently approximate for the purpose.

According to the gas-pressure theory, as usually stated, the pressure exerted should be given by the formula,

$$P = R\theta C'/M = R\theta C/MV, = R\theta C''/MV (1 + C''), \quad (18)$$

where R is the gas-constant and V the volume of unit mass of solution containing C/M gramme-molecules of solute. It is well-known that this gives values of P which are much too small for strong solutions, in fact nearly three times too small for the strongest solutions of cane-sugar tested by Lord Berkeley and Mr. Hartley, as shown by the curve marked I in fig. 5. A better approximation is obtained if V is replaced by the volume of solvent in the solution, namely $(1-C)U$, which gives

$$P = R\theta C/MU (1-C) = R\theta C''/MU. \quad (19)$$

This proceeding is analogous to subtracting the covolume term b from the volume occupied, as in the gas equation of Van der Waals. But even this is not sufficient in the case of cane-sugar, as shown by the straight line marked II in fig. 5. The residual discrepancy may be accounted for by introducing other empirical terms in the equation as indicated by Lord Berkeley in his note *On the Application of Van der Waals' Equation to Solutions*.* This is not altogether satisfactory, because so many different types of equation are possible, and the empirical constants cannot be interpreted, or predicted from other properties of the substances concerned.

The surface-tension and hydrate theories, as usually stated, are unprofitable, because they do not appear to admit of the calculation of the osmotic pressure for comparison with the results of experiment. There is no doubt that differences of surface-energy exist between the solution and solvent, and that molecular complexes are formed in solution, and that such effects might give rise to a difference of pressure, but the relation between the phenomena is not directly capable of numerical expression in any obvious manner.

The vapour-pressure theory is undoubtedly the most practical, because there is a definite and simple relation between the vapour-pressure and the

* 'Roy. Soc. Proc.,' A, vol. 79, p. 125.

osmotic pressure, which has been closely verified by the experiments of Lord Berkeley and Mr. Hartley for strong solutions. It remains to be seen whether the vapour-pressure of a solution can be theoretically related in any simple manner to its molecular constitution. A step in this direction has been made by Poynting,* who supposes that each molecule of the solute combines with a molecules of solvent in such a manner as to render them inactive for evaporation. If there are n molecules of solute to N of solvent in the solution, the ratio of the vapour-pressures p''/p' of solution and solvent should in that case, according to Poynting, be the ratio of the number of free molecules of solvent $N-an$ to the whole number of molecules of solvent N in the solution. We thus obtain the relations

$$p''/p' = (N-an)/N, \quad \text{or} \quad (p' - p'')/p' = an/N. \quad (20)$$

In order to reconcile this assumption with Raoult's law for dilute solutions of non-electrolytes, it is necessary to suppose that $a = 1$, or that each molecule of solute combines with only *one* molecule of solvent. Since $n = C/M$ and $N = (1-C)/m$, where M, m are the molecular weights of the solute in solution and of the vapour of the solvent respectively, we obtain immediately by substitution in (2) or (3), putting $v = R\theta/mp$ and $V = U$, the approximate result (19), which is equivalent to that given by Poynting. But Poynting applies the assumption only to dilute solutions, and does not, therefore, distinguish between U, V , and W .

The advantage of making this assumption with regard to the variation of the vapour-pressure with the number of free molecules is that it gives a comparatively simple explanation, without straining the gas-pressure analogy, of the fact that the osmotic pressure appears to depend more nearly on the volume occupied by the solvent in the solution than on the whole volume of the solution. The particular assumption made does not, however, appear to be quite satisfactory for two reasons: (1) it does not represent the results of experiment sufficiently closely for strong solutions, and (2) it is necessary to suppose that each molecule combines with only *one* molecule of solvent. If each molecule of the solute combines with two or three or more molecules of solvent, the change of vapour-pressure and the depression of the freezing-point, on Poynting's assumption, would be twofold or threefold, or in proportion to the number of molecules to each molecule of solute. At first sight this would give a natural explanation on the association theory of the case of electrolytes, if there were not so much conclusive evidence that the effect in this case is due to dissociation or multiplication of molecules. The existence of multiple hydrates would rather lead one to expect that the molecular

* 'Phil. Mag.,' vol. 42, p. 298, 1896.

complexes occurring in solutions often contain several molecules of solvent, and that the number of molecules of solvent in each complex may vary considerably without producing so marked an effect on the vapour-pressure or the freezing-point as would be indicated by Poynting's theory.

A more natural assumption to make with regard to the dependence of the vapour-pressure on the number of molecules in the solution would appear to be that the vapour-pressure ratio p''/p' is equal to the ratio of the number of free molecules of solvent to the whole number of molecules in the solution, instead of to the number of molecules of solvent. On this view, each molecular complex is treated as a single molecule, and it is immaterial, to a first approximation, how many molecules of solvent it may contain. If each molecule of solute appropriates a molecules of solvent, and if n, N denote, as before, the whole number of molecules of solute and solvent respectively in the solution, the number of free molecules of solvent is $N-an$, and the whole number of molecules in solution is $N-an+n$. We thus obtain,

$$\begin{array}{ll} \text{Ratio of Vapour-Pressures} & p''/p' = (N-an)/(N-an+n), \\ \text{Relative Lowering of Vapour-Pressure} & (p'-p'')/p' = n/(N-an+n), \\ \text{Lowering Relative to Solution} & (p'-p'')/p'' = n/(N-an). \end{array} \quad (21)$$

This agrees with Poynting's assumption in the special case where $a=1$, and coincides with Van't Hoff's theory in the limit for dilute solutions, *whatever be the value of a* . But it makes a very considerable difference in the case of strong solutions. In applying the assumption $p'/p'' = (N-an+n)/(N-an)$ to strong solutions, it is necessary to employ the logarithmic formula (10), namely, $P'_0 U_0 = R\theta \log_e(p'/p'')/m$, in place of the approximate formula (2). The curves in fig. 5 are drawn to represent the values of the osmotic pressure for the two cases $a=2$ and $a=5$, which appear to represent the observations on dextrose and cane-sugar within the limits of experimental error. The product PU is plotted in place of P , because the correction for U is small and somewhat doubtful, and was not applied by Lord Berkeley and Mr. Hartley. The highest points for cane-sugar at $n=7.6$ lie below the curve, but the agreement is sufficiently close to suggest that the formation of molecular complexes containing several molecules of solvent is a very probable explanation of the main features of the variation of osmotic pressure with concentration in solutions of the same kind as those of cane-sugar.

It will be observed that since $\log_e(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 \dots$, the expression for the osmotic pressure reduces approximately to the form

$$P = R\theta n/(N-an) Um, \quad (22)$$

when n is small compared with $N-an$. Here U_m is the volume occupied by 1 gramme-molecule of the solvent in the solution; $N-an$ is the number of free molecules of the solvent in the solution to n of the solute. The osmotic pressure is therefore approximately equal to that which would be exerted by n molecules of gas in the volume occupied by the remaining free molecules of the solvent. The gas-pressure analogy still holds to this extent as a first approximation, even in fairly strong solutions. But it would be straining the analogy unduly to regard the pressure which the molecules would exert in an imaginary volume if they were gaseous as being the primary cause of the phenomena of osmotic pressure. In reality the equilibrium depends primarily on equality of vapour-pressure. If vapour is supplied to a solution at a pressure in excess of the normal vapour-pressure of the solution, the vapour will condense in the solution, and the condensation will continue until either the pressure, or the temperature, or the concentration of the solution, is changed in such a manner as to restore equilibrium between the solution and the vapour. The assumption of a simple molecular relation for the vapour-pressure seems also to give better agreement with experiment than the assumption of a similar relation for the gas-pressure.

Lowering of the Freezing-point in Strong Solutions.

13. Direct measurements of the vapour-pressure or osmotic pressure in strong solutions are very difficult, and there is little material available for testing the theory in this direction. Observations of the lowering of the freezing-point are more numerous, and less liable to serious error, although they present considerable difficulties in the case of strong solutions. In the usual case of the solvent separating out in the pure state on freezing, the vapour-pressure of the solution at the freezing-point must be equal to that of the solid solvent. Taking the case of aqueous solutions for simplicity of description, in order to find the osmotic pressure of a solution at its freezing-point we have merely to substitute the value p of the vapour-pressure of ice in place of p'' , the vapour-pressure of the solution in formula (10) for the osmotic pressure. The determination of vapour-pressure, or molecular weight, or osmotic pressure, by the freezing-point method depends, therefore, primarily on knowing the relation between the vapour-pressures of ice and water below the freezing-point.

The difference of vapour-pressures $p-p'$ of ice and water at a temperature θ° C. near the freezing-point 0° C. is generally obtained from Kirchhoff's approximate formula,

$$dp/d\theta - dp'/d\theta = L/\theta v, \quad (23)$$

where L is the latent heat of fusion, and v the volume of the vapour. Putting $p-p'$ for $dp-dp'$, and t for $d\theta$, and substituting $v = R\theta_0/mp'$, we obtain,

$$(p-p')/p' = +mLt/R\theta_0^2. \quad (24)$$

Equating this to the approximate formula for the relative lowering of the vapour-pressure of the solution $(p'-p'')/p'$ in terms of the osmotic pressure and the concentration, we have the usual relation

$$mPU/R\theta = n/N = mC''/M = -mLt/R\theta_0^2 = -2.64t/\theta_0. \quad (I)$$

This gives for the "molecular lowering" of the freezing-point produced by 1 gramme-molecule of solute in 100 grammes of solvent, in the case of water, the value $t_m = 18^\circ.6$, or for 1 gramme-molecule in 100 *gramme-molecules* of water the value $t = 1^\circ.033$, if L is taken as 79.5 calories, and $R = 1.98$ calories.

Results for the lowering of the freezing-point in strong solutions are generally compared by tabulating the molecular lowering deduced from different ranges of temperature, for comparison with the approximate result given by this formula. This method illustrates the wide divergence of the experimental results from the approximate formula, but it does not throw much light on the causes of the divergence, because the approximate formula deduced on such assumptions could not be expected to hold at all accurately except in the immediate neighbourhood of the freezing-point.

The formula tacitly assumes that the ratio of the difference of vapour-pressures of ice and water to the vapour-pressure of water is directly proportional to t . To give some idea of the error involved in the case of strong solutions, the values of $\log_e (p'/p)$ calculated on this assumption are tabulated under the heading I in the accompanying Table II, for comparison with the values given by more accurate formulæ.

A method adopted in many books is to integrate Kirchhoff's equation on the assumption that the latent heat of fusion L , or rather the difference of the latent heats of vaporisation of the solid and liquid, is constant, which leads at once to the result,

$$\log_e (p'/p) = -mLt/R\theta\theta_0, = -2.64t/\theta. \quad (II)$$

This fits very well with formula (10) for the osmotic pressure, giving the simple expression $PU = Lt/\theta_0$, but since the specific heats of water and ice are known to differ considerably, the values to which it leads are probably quite as much in error as those deduced on the first assumption. The resulting values of $\log_e (p'/p)$ are given in the table under the heading II, and are seen to differ from those given by I by about 8 per cent. at -10°C . and about 16 per cent. at -20°C . The equation is no doubt preferable to I

as corresponding to a simple and definite assumption, but as the assumption is certainly wrong, it would be futile to apply the equation to strong solutions.

Accurate Equation for the Vapour-pressures of Ice and Water in terms of the Specific Heats.

14. In order to obtain a more accurate equation it is necessary to take account of the difference of the specific heats, which corresponds to the variation of the latent heat of fusion. This may be done in many ways, but it affords a good example of the circuit method. Imagine a circuit consisting of parallel columns of ice and water, AB, CD, in equilibrium at either end with vapour at 0°C ., and vapour at $-t^\circ\text{C}$., as indicated in fig. 6. Suppose:

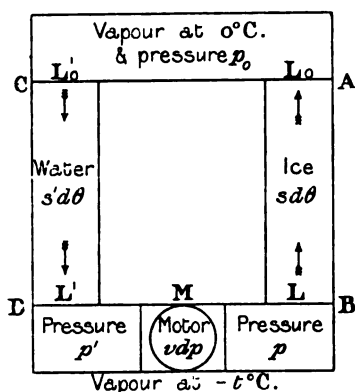


FIG. 6.—Circuit Method for Ratio of Vapour-pressures of Ice and Water in terms of the Specific Heats.

unit mass to travel round the circuit in the direction indicated, starting with the state of vapour at 0°C . under the vapour pressure p_0 , which is the same for ice and water. Heat L'_0 is evolved in condensation to water at 0°C . Heat $s'd\theta$ is evolved in cooling for each element $d\theta$ from 0° to $-t^\circ$, where s' is the specific heat of water under vapour-pressure p' . Heat L' is absorbed in evaporation at $-t$ at a pressure p' . The vapour is then expanded through a motor M at constant temperature $-t$ to a pressure p , the vapour-pressure of ice at $-t$. The work done in the motor is the integral of $v dp$, and is equal to the heat absorbed. Heat L is evolved in condensation to ice at $-t$. The integral of $s d\theta$ is absorbed in heating to 0°C ., where s is the specific heat of ice under its own vapour-pressure p . Finally, heat L_0 is absorbed in evaporation at 0°C . The work done by the expansion of the solid or liquid may be neglected, because the pressures are very low and the volumes of the solid and liquid are quite negligible compared with that of the vapour.

By the first law, equating the heat absorbed to the work done, we obtain,

$$(L-L')-(L_0-L'_0)=\int_{\theta_0}^{\theta}(s'-s)d\theta. \quad (25)$$

By the second law, taking the integral of dH/θ round the circuit,

$$(L-L')/\theta-(L_0-L'_0)/\theta_0=\int_{\theta_0}^{\theta}(s'-s)d\theta/\theta+\int_p^{p'}vdp/\theta. \quad (26)$$

Substituting from (25) in (26) for $L-L'$, and putting L_f the latent heat of fusion at 0° C., for the difference of the latent heats of vaporisation at 0° , we obtain the required relation in terms of L_f and the specific heats,

$$R \log_e(p'/p)/m = -L_f t/\theta\theta_0 + \frac{1}{\theta} \int_{\theta_0}^{\theta}(s'-s)d\theta - \int_{\theta_0}^{\theta}(s'-s)d\theta/\theta. \quad (27)$$

This result is equivalent to equation II with added terms representing the effect of the difference of the specific heats. The integrals cannot be evaluated exactly without a knowledge of the mode of variation of the specific heat with temperature, but we shall evidently obtain a much better approximation than either I or II if we assume $(s'-s)$ constant and equal to its value at 0° C. The most probable value of the difference of the specific heats of ice and water at 0° C. appears to be $(s'-s)=0.52$. Putting $L_f=79.5$, $R/m=0.1103$, and $\theta_0=273$, we obtain the numerical formula,

$$\log_e(p'/p) = -2.64t/\theta + 4.71(t/\theta - \log_e(\theta/\theta_0)). \quad (III)$$

The first term is the same as in II. The second term, depending on the specific heats, is small because t/θ is nearly equal to $\log_e(\theta/\theta_0)$ when t is small. Its value to a first approximation is $-2.35(t/\theta_0)^2$. Values deduced from this formula are given in column III. They lie nearly midway between those given by I and II.

The mode of variation of the specific heat of water at temperatures below 0° C. cannot be determined satisfactorily by experiment. It probably increases with fall of temperature, being continuous with the curve above 0° C. The specific heat of ice appears to diminish with fall of temperature. Regnault finds the value $s=0.462$ for ice (corrected) between 0° and -78° C. Nordmeyer and Bernouilli give 0.345 between 0° and -185° . The probable error involved in neglecting the variation of the specific heat is small, and can be estimated by making different assumptions. If we suppose for instance that the difference of the specific heats varies *directly* as the absolute temperature, or that $(s'-s)=s_0\theta/\theta_0$, we obtain the simple result,

$$R \log_e(p'/p)/m = -L_f t/\theta\theta_0 - s_0 t^2/2\theta\theta_0. \quad (28)$$

If $s_0=0.52$, this gives the numerical formula,

$$\log_e(p'/p) = -2.64t/\theta - 0.0172t^2/2\theta. \quad (IV)$$

If, on the other hand, we make the exactly opposite assumption, that $(s' - s)$ varies *inversely* as θ , or $s' - s = 0.52\theta_0/\theta$, we obtain the equation,

$$\log_e(p'/p) = -2.64 t/\theta - 4.71 (t/\theta - (\theta_0/\theta) \log_e(\theta/\theta_0)). \quad (V)$$

Values calculated by these formulæ are given in columns IV and V. The differences from column III are probably within the limits of error of our knowledge of the specific heats at 0° C. The absolute value of $(s' - s)$ is more important for our purpose than a knowledge of the mode of variation.

It will be observed in comparing the values of $\log_e(p'/p)$ in columns III, IV, and V, with the values of $-2.64 t/\theta_0$ given in column VI, that they are very nearly equal; the differences average about 0.5 per cent. down to -50° C. The values are all very nearly proportional to t , at least within the limits of possible error of our knowledge of $(s' - s)$. If we might assume $s_0 = 2L_f/\theta_0 = 0.582$, in (28), or $(L - L')/\theta^2 = L_f/\theta_0^2$, the equation would reduce *exactly* to the very simple form

$$\log_e(p'/p) = -2.64 t/\theta_0, \quad (VI)$$

which is the same as II, except that θ is replaced by θ_0 . This requires a rather smaller value for the specific heat of ice than that usually accepted, but considering the uncertainty of our knowledge of the specific heats, this formula has been adopted in the calculations for the sake of simplicity, as it has a definite theoretical basis, and agrees with III or IV within the probable limits of error of experiment. In many cases formula V, which allows for the probable increase of $(s' - s)$ with fall of temperature, appears to give better agreement with experiment, and it may eventually prove to be a better approximation than the simpler formula VI.

Table II.—Values of $\log_e(p'/p)$ for Ice and Water according to Formulæ I—VI.

| t. | I. | II. | III. | IV. | V. | VI. | (p'/p). |
|-----|---------|---------|---------|---------|---------|---------|---------|
| 0. | | | | | | | |
| — 2 | 0.01915 | 0.01948 | 0.01935 | 0.01935 | 0.01935 | 0.01934 | 1.01953 |
| — 5 | 0.04721 | 0.04924 | 0.04842 | 0.04843 | 0.04842 | 0.04835 | 1.04955 |
| — 7 | 0.06548 | 0.06948 | 0.06787 | 0.06790 | 0.06786 | 0.06769 | 1.07004 |
| —10 | 0.09229 | 0.10037 | 0.09705 | 0.09711 | 0.09701 | 0.09670 | 1.10154 |
| —18 | 0.11840 | 0.13200 | 0.12631 | 0.12638 | 0.12622 | 0.12571 | 1.13397 |
| —15 | 0.13543 | 0.15348 | 0.14581 | 0.14596 | 0.14567 | 0.14505 | 1.15611 |
| —20 | 0.17680 | 0.20870 | 0.19470 | 0.19500 | 0.19440 | 0.19340 | 1.21340 |
| —30 | 0.25463 | 0.3269 | 0.2927 | 0.2939 | 0.2914 | 0.2901 | 1.33660 |
| —40 | 0.3269 | 0.4535 | 0.3918 | 0.3945 | 0.3876 | 0.3868 | 1.47231 |
| —50 | 0.4044 | 0.5930 | 0.4896 | 0.4963 | 0.4828 | 0.4835 | 1.62181 |
| —60 | 0.4575 | 0.7435 | 0.5858 | 0.5977 | 0.5719 | 0.5802 | 1.78649 |

The last column contains the value of the ratio of the vapour-pressures of water and ice required for calculating the lowering of the freezing-point by the rule for the vapour-pressure of a solution given in equations (21). It may be remarked that this ratio cannot be taken from tabulated values of the vapour-pressures of water and ice, such as those given in Landolt and Börnstein's tables (based partly on the work of Thiesen and Scheel), because the vapour-pressures of water below the freezing-point cannot be determined experimentally with sufficient accuracy for the purpose, since the difference of vapour-pressure is very small. Thus the ratio of the vapour-pressures at -2° C. from the tables is 1.0164, and the required difference 0.0164 is about 15 per cent. too small. But the tabulated vapour-pressures for ice agree with those calculated by the author's method* to within a few thousandths of a millimetre, on the assumption that its specific heat is 0.48 and equal to that of steam.

Application to Non-Electrolytes.

15. In order to apply this table to the lowering of the freezing-point of a solution, the values of $p'/p - 1$, taken from the last column, multiplied by 100, are plotted against the corresponding values of t in the diagram, fig. 7, and give the curve marked $a = 0$. The same curve, if the abscissa is taken to represent n , the number of molecules of solute to $N = 100$ of solvent, should give the depression of the freezing-point for a solution for which $(p' - p'')/p'' = n/N$, that is to say for the case in which $a = 0$ in equations (21), or the solute does not combine with any molecules of solvent. The curves for different values of a are found from the curve $a = 0$ by calculating the values of the ratio $(p' - p'')/p'' = n/(N - an)$, finding the corresponding values of t from the vapour-pressure curve $a = 0$, and plotting the values so found against n .

The straight line $t = -1.033n$ is the tangent at 0° C. to the vapour-pressure curve $a = 0$, and represents the value of the depression of the freezing-point for a normal substance according to Van't Hoff's cryoscopic constant $k = 18^{\circ}.6$ for 1 molecule of solute in 100 grammes of solvent. It gives a fair approximation to the curve of vapour-pressure for weak solutions, the error at $t = -10^{\circ}$ being less than 5 per cent. It may be necessary to point out that this assumption differs widely from the assumption of a cryoscopic constant for *volume-normal* solutions (gramme-molecules per litre) which is often made in reducing freezing-point observations according to the gas-

* 'Roy. Soc. Proc.,' June, 1900. The vapour-pressures of water below the freezing-point are often calculated from Regnault's formula for the latent heat, which appears (*loc. cit.*) to be inaccurate.

ure theory. The curve so obtained depends on the density of the solution, is different for different substances. If the depression of the freezing-point for solutions of cane-sugar were proportional to the number of gramme-molecules per litre, we should obtain the curve marked I in fig. 7, which illustrates the danger of pushing an attractive analogy too far. The depression calculated on the gas-pressure theory would be $3^{\circ}72$ for a solution containing gramme-molecules of sugar per litre, as against $6^{\circ}6$ if the depression is

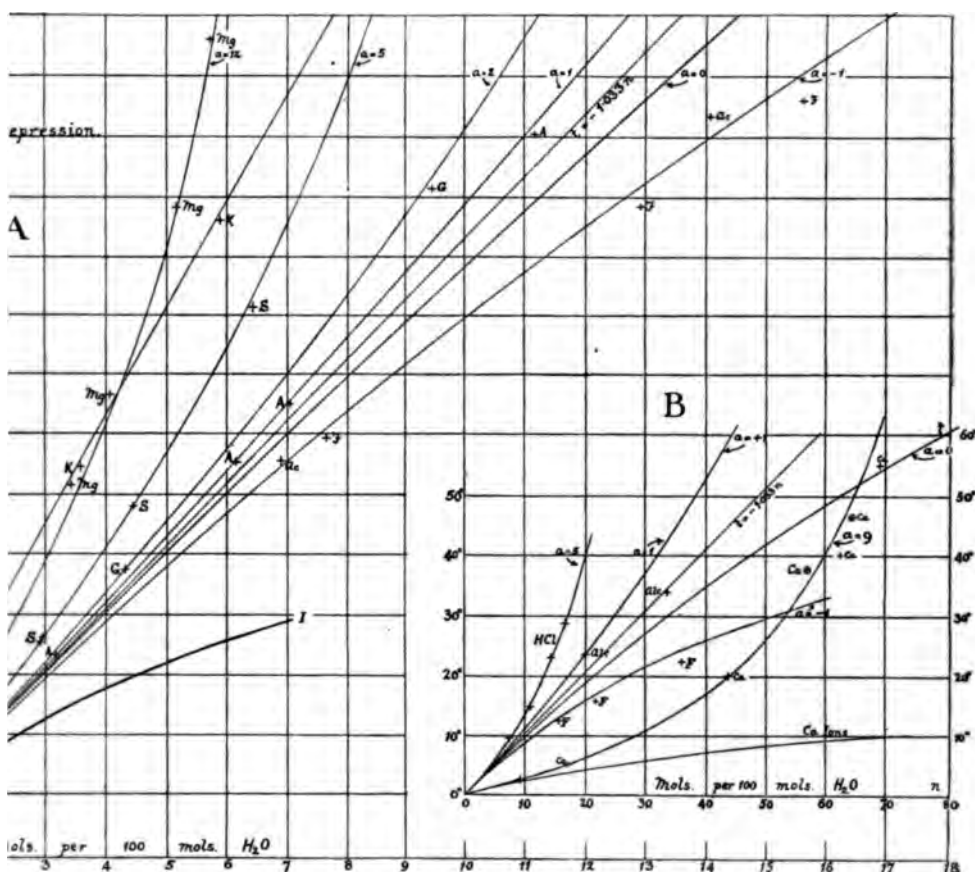


FIG. 7.—Depression of the Freezing-point in Aqueous Solutions.

proportional to n/N . Experiment gives $9^{\circ}15$, according to Jones and Getman. The gas-pressure theory is inconvenient, because it involves considerations of density, and it fails to represent the observations satisfactorily, even for dilute solutions, because it gives in many cases so bad an approximation to the vapour-pressure curve.

The crosses marked S, representing the observations on the depression of the freezing-point for cane-sugar, agree very well with the curve marked

$\alpha = 5$, as in the case of the osmotic pressure. Thus the observed depression at $n = 6.41$ is $t = -9^{\circ}.15$. The calculated value for $\alpha = 5$ is $t = -9^{\circ}.30$. Van't Hoff's rule gives $t = -6^{\circ}.60$. For $\alpha = 0$ the depression would be $t = -6^{\circ}.42$. The depressions recorded in Landolt and Börnstein's tables for methyl and ethyl alcohols, marked A in fig. 7A, agree very well with the curve marked $\alpha = 1$, up to $n = 20$ molecules per 100 of solvent. One observation for ethyl alcohol in fig. 7B, at $n = 33.7$, lies entirely off the curve.

[*Note added April 13, 1908.*—Guthrie's observations* on the freezing of alcohol solutions appear to indicate that a hydrate may separate in place of pure ice when $n = 20$, giving rise to a discontinuity in the F. P. curve. Analysis of his observations down to -65° C. indicates a third branch extending from $n = 42$ to $n = 90$, but the temperatures in this region are probably not very accurate. The ice branch, giving $\alpha = 1$, can be traced as far as $n = 25$, in the absence of the first hydrate.]

The values for glycerine (G) agree with the curve marked $\alpha = 2$. The freezing-points for acetone (Ac) and formic acid (F) lie *below* the curve $\alpha = 0$, in a manner which suggests that the dissolved molecules associate with each other in solution according to a similar law, as the points representing the observations lie very symmetrically on either side of the curve marked $\alpha = -1$.

Application to Electrolytes.

16. In applying the theory to electrolytic solutions, we are met by the difficulty that the molecules are dissociated to a variable extent depending on the dilution. The degree of dissociation is usually inferred from the ratio of the molecular electric conductivity of the solution to that at infinite dilution. It is very doubtful what this ratio really represents in the case of strongly dissociated electrolytes, as the free ions are so numerous that they must interfere very greatly with each others' movements. It is possible that the dissociation is really much greater than that calculated in this manner, but the ratio may nevertheless represent the *effective* number of free molecules from the point of view of depression of the freezing-point as well as from the point of view of electric conductivity. Adopting this hypothesis, if $n'' = (1 + k/k_0)n$ is the effective number of molecules, where k/k_0 is the ratio of k , the molecular conductivity of the solution, to its limiting value k_0 when $n = 0$, for a binary electrolyte, the required value of the vapour-pressure ratio $(p' - p'')/p''$ should be $n''/(N - an'')$. The corresponding depression t is

* F. Guthrie, 'Phys. Soc. Proc.,' vol. 1, p. 53, 1874.

taken from the vapour-pressure curve $a = 0$ and plotted against n . The results for HCl so far as they go, up to a depression of 29° , agree very well with this hypothesis, taking $a = 5$. They are plotted in the small scale diagram (fig. 7B), and the values of n are doubled to make the initial slope agree with the curve $a = 0$. Thus the observed depression $t = 28^\circ.8$ corresponds with an actual strength $n/N = 8.39/100$, but is plotted against $2n = 16.78$. The curve would otherwise be too steep.

The observations of Roozeboom* for CaCl_2 , treated in a similar manner, allowing for the fact that it dissociates into three ions, agree very well with $a = 9$. To avoid confusion the curve is plotted against $10n$. Thus the observed depression $t = -20^\circ$, corresponding to $n/N = 4.37/100$, is plotted against 43.7 . The two highest points, at $t = 40^\circ$ and 55° , lie somewhat off the curve, but accurate observations here would be very difficult, and the ionisation is uncertain. At $t = -55^\circ$, $n = 6.92$, and $n' = 9.80$, Van't Hoff's rule, indicated by the curve marked Ca Ions, would give a depression of only 10° . The present rule gives $t = -61^\circ$, which is more nearly of the right order of magnitude, and illustrates the great influence of the hydration factor a . CaCl_2 is known to form hydrates containing a large number of water molecules. The usual hydrate contains six molecules. It is quite likely that it would take to itself three others in solution. The osmotic pressure at -61° , according to the formula (10), would be about 600 atmospheres. Taking $(p' - p'')/p'' = n''/(N - an'')$ the osmotic pressure would be infinite when $n'' = 11.1$, or $an'' = 100$. The solution would avoid this difficulty by crystallising, or by a change in the value of a . It is probable that mixtures of molecular complexes corresponding to different values of a may occur in very strong solutions.

The observations (Mg), fig. 7A, on the depression of the freezing-point of solutions of MgCl_2 , given in Landolt's tables, do not extend beyond $t = -13^\circ.61$, but so far as they go they indicate a value $a = 12$ for the number of H_2O molecules in each complex. Owing to the steepness of the curve, the observed depressions are plotted against the values of n doubled.

The curve (K) for KCl, which is of quite a different character, agrees very well with the degree of ionisation deduced from the electric conductivity, on the hypothesis that each of the n'' molecules takes one molecule of water. The curve for NaCl would coincide very closely with that for KCl if each molecule of NaCl took two molecules of H_2O , but the observations for NaCl do not appear to extend beyond $n = 1.8$. In plotting these observations is not doubled and the initial slope is 2.066 owing to the ionisation.

* 'Zeit. Phys. Chem.,' vol. 4, p. 42, 1889.

Rise of the Boiling-point.

17. The rise of the boiling-point affords a means of verifying the theory at a different temperature, but the method is more difficult of application, and the available observations less numerous than in the case of the depression of the freezing-point. Kahlenberg's data for cane-sugar, KCl and NaCl,* are

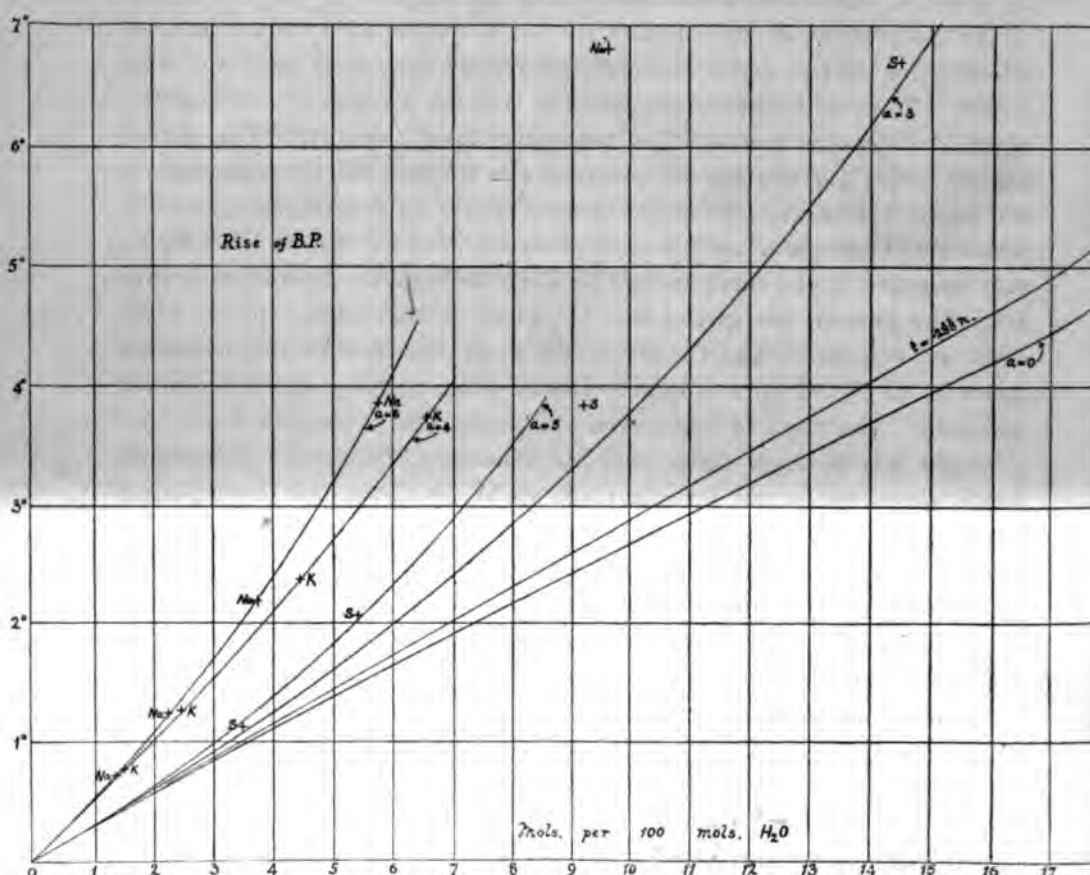


FIG. 8.—Rise of the Boiling-point in Aqueous Solutions.

plotted in the diagram, fig. 8. The curve $a = 0$ gives the relation between the vapour-pressure ratio $(p' - p'')/p''$ and the rise of temperature t above the boiling-point. The straight line $t = 0.288 n$ corresponds to Van't Hoff's ebullioscopic constant, the error of which is about 8 per cent. at $n = 10$. The observations (S) on the rise of the boiling-point for solutions of cane-

* L. Kahlenberg, 'Journ. Phys. Chem.,' vol. 5, p. 362, 1901.

sugar agree very fairly with the curve $a = 5$ up to a concentration of between 5 and 6 molecules of sugar to 100 of H_2O , which is about the limit of good agreement in fig. 5. It is perhaps remarkable that the number of H_2O molecules to one of sugar should apparently be the same at 100°C . as at 0°C . Beyond this point, as in fig. 5, the degree of hydration a appears to diminish, being about 4 on the average at $n = 9$, and 3 at $n = 15$. This is perhaps to be expected, as the mass of the sugar at $n = 15$ is about three times the mass of the water present, and the osmotic pressure, when the rise of the boiling-point is $6^\circ\cdot7$, is about 405 atmospheres.

No data appear to exist for the dissociation of electrolytes at or above 100°C . It is probable, however, that the dissociation does not change very greatly with temperature. The enormous increase in the conductivity of electrolytes with rise of temperature is to be explained chiefly by diminution of viscosity. Taking Kahlenberg's data for the dissociation of KCl and NaCl at 95°C ., the observations (K) on the elevation of the B.P. for solutions of KCl agree very well with the vapour-pressure theory, if $a = 4$, so far as the data for the dissociation extend, namely up to $n = 6\cdot5$. Beyond this point there is one observation at $n = 11\cdot82$, $t = 7\cdot60$, which appears to lie nearly on a continuation of the same curve. The observations for NaCl (Na) agree very well with the curve $a = 6$, up to $n = 6$. The highest point, at $n = 9\cdot63$, lies below the curve. The discrepancy may be due to errors of observation, or may indicate a systematic divergence. The agreement is much better than would be expected considering the difficulty of the observations, and the uncertainty of the dissociation data. It is noteworthy that both KCl and NaCl appear to annex many more molecules of H_2O at 100°C . than at 0°C . The dissociation data for the other electrolytes examined by Kahlenberg do not extend sufficiently far to be applicable.

Effect of the Heat of Dilution.

18. It is important to enquire how far the simple and convenient assumption made with regard to the dependence of vapour-pressure of a solution on its concentration is consistent with thermodynamical principles. The variation of the vapour-pressure of a solution with temperature is readily obtained by the circuit method in terms of the latent heat of vaporisation. What we require in the present case is the variation of the ratio p'/p'' of the vapour-pressures of solvent and solution. This is immediately given by a circuit similar to fig. 6 in which the branch AB representing ice is replaced by solution. Since the vapour-pressures of solution and solvent are not the same at θ_0 , we must insert an additional motor in the branch AC.

If double dashes, as usual, refer to the solution, and single dashes to the solvent, we thus obtain the equations,

$$(L''-L')-(L_0''-L_0') = \int_{\theta_0}^{\theta} (s'-s'') d\theta, \quad (29)$$

$$(L''-L')/\theta-(L_0-L_0')/\theta_0 = \int_{\theta_0}^{\theta} (s'-s'') d\theta/\theta + \int_{p''}^{p'} v dp/\theta - \int_{p_0''}^{p_0'} v dp/\theta_0. \quad (30)$$

Since $L''-L' = Q$ (§ 11), the heat evolved on dilution per unit mass of solvent added, the first equation gives the variation of the heat of dilution with temperature in terms of the difference of the specific heats of the pure solvent s' , and of the solvent in solution, which is represented by s'' . Writing $q = dQ/d\theta$ as an abbreviation for $s'-s''$, we obtain the required equation of vapour-pressure in terms of Q and q ,

$$(R/m)(\log_e(p'/p'')-\log_e(p_0'/p_0'')) = -Q_0t/\theta\theta_0 + \frac{1}{\theta} \int_{\theta_0}^{\theta} q d\theta - \int_{\theta_0}^{\theta} q d\theta/\theta, \quad (31)$$

where Q_0 is the latent heat of dilution at θ_0 .

We observe immediately that the ratio p'/p'' cannot be constant unless Q is zero. This is a well-known result, and is approximately true for solutions of many substances. For such substances it is perfectly justifiable to employ the vapour-pressure relation $(p'-p'')/p'' = n/(N-an)$, and it is highly probable that the hydration factor a will not vary greatly with temperature or with concentration, as we have seen to be the case with solutions of cane-sugar.

If Q is not zero, equation (31) gives a condition which must be satisfied by corresponding variations of a or n . In many solutions the number of effective molecules n'' varies continuously with temperature according to the degree of association or dissociation of the molecules of the solute. The factor a may also vary, but it appears in general to have a simple integral value which remains constant for considerable ranges of concentration and temperature, as we have seen in the case of electrolytes.

Equation (31), like the analogous equation for the ratio of the vapour-pressures of ice and water, may take a variety of forms according to the mode in which Q varies with temperature. If Q is constant, or $q = 0$, the equation reduces to a form similar to that commonly employed by physical chemists for deducing heats of solution from observations of solubility, or *vice versa*. The two cases are evidently very closely analogous, and the solubility equation may be deduced by the circuit method in a precisely similar way. Substituting for the vapour-pressure in terms of the osmotic pressure from equation (10), we obtain in this case for the variation of the osmotic pressure with temperature,

$$PU/\theta - P_0U_0/\theta_0 = -Q_0t/\theta\theta_0.$$

The osmotic pressure will not be proportional to the absolute temperature if $Q = 0$, unless U is also constant. But the proportionality may hold even if Q is not zero, provided that U varies in a suitable manner.

If q is not zero, we obtain solutions like (IV), (V), and (VI) for the vapour-pressures of ice and water, by making corresponding assumptions for q , and the form of the solution may vary widely from that usually assumed. Another case of special simplicity is that in which Q varies as θ , or $q = Q_0/\theta_0$, which gives

$$\log_e(p'/p'') - \log_e(p_0'/p_0'') = -(mq/R) \log_e(\theta/\theta_0),$$

in which case the ratio of the vapour-pressures varies inversely as $\theta^{mq/R}$.

We may further observe that if Q is constant, PU is a linear function of θ , though not proportional to θ , thus,

$$PU = P_0U_0 + (P_0U_0 - Q_0)t/\theta_0,$$

and that if $q = 2Q_0\theta/\theta_0^2$, as in equation (VI) for the vapour-pressures of ice and water, PU is a quadratic function of t , namely,

$$PU = P_0U_0 + (P_0U_0 - Q_0)t/\theta_0 - Q_0(t/\theta_0)^2.$$

It is useful to remember the physical meaning of the coefficients in these expressions, which might naturally be applied to represent the variation of the osmotic pressure with temperature. It also follows from the first expression that if Q is constant and equal to P_0U_0 , the product PU will be independent of the temperature, to the degree of approximation represented by equation (10).

Heat of Dilution and Ionisation of HCl.

19. As an example of the order of magnitude of the effects to be expected, we may take the case of solutions of HCl, for which the heat of dilution is one of the largest known. The quantities actually observed in a calorimetric experiment are the integral heats of solution and dilution obtained by making a solution of known composition and diluting with finite quantities of solvent, involving considerable changes in the concentration. The heat of dilution Q for an infinitesimal change, required in equation (31), may be deduced from the calorimetric observations as follows. By plotting the quantities of heat liberated when 1 gramme-molecule of solute is dissolved in X gramme-molecules of solvent (which is the way in which the observations are generally recorded) against the concentration C'' in grammes of solute per gramme of solvent, or against n/N for the resulting solution, we obtain the total heat of formation of the solution

Q'/n per gramme-molecule of solute as a function of the concentration C'' or n/N . In the case of HCl the curve is very nearly a straight line,*

$$Q'/n = 17,340 - 5920 C'' = 17,340 - 12,000 n/N. \quad (32)$$

The heat of solution at concentration n/N , or the heat evolved on adding a small quantity dn to a large mass of solution per gramme-molecule added, is represented by dQ'/dn , and is given by the equation,

$$Q'' = dQ'/dn = 17,340 - 24,000 n/N. \quad (33)$$

The heat of dilution at concentration n/N , or the heat evolved on adding a small quantity of solvent dN to a large mass of solution per gramme-molecule added, is represented by $Q = dQ'/dN$, and is given by the equation,

$$Q = dQ'/dN = +12,000 (n/N)^2. \quad (34)$$

If n molecules of solute are added to a large quantity of solution of concentration n/N , the heat evolved is nQ'' . If N molecules of solvent are added, the heat evolved is NQ . The sum of these two operations must be equal to the heat of formation Q' of a quantity of solution containing n molecules of solute to N of solvent. In other words, we have the relation $NQ + nQ'' = Q'$, which is evidently[†] satisfied.

The heat of dilution Q , which is the quantity with which we are immediately concerned, is very large in the case of HCl, but is given by a very simple expression. In other cases, *e.g.*, H_2SO_4 , the curve is less simple, but may generally be represented as consisting of straight lines, which probably correspond to the formation of different hydrates or ions.

In the case of HCl, the depression of the freezing-point is approximately 40° for a solution for which $n = 10$ and $N = 100$. By equation (34) the heat evolved is 120 calories when 1 gramme-molecule of water is added to a large quantity of solution of this concentration. The heat evolved *per gramme* of water added, which is denoted by Q in equation (31) (deduced by taking *unit mass* of solvent round the circuit), is 6.67 calories. We see that, even in this very extreme case, the heat of dilution is a comparatively small fraction of the latent heat of fusion, namely, 79.5 calories, and will not greatly influence the curve of vapour-pressure. For dilute solutions, the effect will in any case be practically negligible, since it varies as the square of the concentration.

Since evolution of heat in any case is mainly connected with combination or dissociation of molecules, it is not at all unlikely that the heat of dilution may be accounted for in the majority of cases by the change in the

* The observations appear to have been smoothed to agree with Thomsen's hyperbolic formula, which inverts into the straight line above given.

effective number of molecules n'' in the vapour-pressure formula. This would account to a great extent for the surprisingly good agreement obtained in the case of electrolytes on the assumption $\alpha = \text{constant}$. It may be remarked that the agreement obtained in any case depends greatly on taking values of the ionisation as near the required temperature as possible. As might naturally be expected, the agreement of the observations at 100°C. is greatly impaired if values of the ionisation at 18°C. are taken. On the other hand, the agreement of the observations on the depression of the freezing-point is considerably improved, especially for dilute solutions, if values of the ionisation at 0°C. are employed in place of the values at 18°C. Values of the ionisation at 18°C. were at first employed in constructing the diagram, fig. 7, as being the more accurate, and more readily accessible. It did not appear to be worth while to redraw the curves employing the data for the ionisation at 0°C. when accessible, because the data were incomplete, and because the general conclusions remained unaltered. Although the agreement with theory was in many cases greatly improved, the uncertainty of the result for large values of the depression still remained.

The relation of the heat of dilution to the heat of ionisation and hydration is a most important and interesting question, but the data do not appear to be sufficiently complete, and it would be better to postpone the discussion of this point.

On the Hydrate Theory of Solution.

20. The theory of vapour-pressure and osmotic pressure outlined in this paper appears to afford the most direct method hitherto proposed of calculating the composition of definite molecular compounds, analogous to hydrates, occurring in solutions. The hypothesis apparently permits the extension, in a slightly modified form, to strong solutions of general principles which have hitherto been applicable only to dilute solutions. The existence of hydrates in solution has often been maintained, and has been supported by much indirect experimental evidence, but the theory has usually been stated in a manner which was open to serious objection. The essential point of a hydrate theory (as opposed to a diffusion-, or solution-pressure-, or gas-pressure-, or variable-aggregation theory) is the formation of definite hydrates according to the fundamental law of chemical combination. The difficulty of such a theory has been to determine the value of the hydration factor α , and to show that it was constant within certain limits, and equal to a simple integer. I have endeavoured to indicate how this may be determined, and I think I may fairly claim to have made out a good *prima facie* case for a modified form of the hydrate theory.

The problem has recently been attacked by H. C. Jones and his assistants at Johns Hopkins University, from a study of the depression of the freezing-points of strong solutions. They have accumulated a great deal of material, but I cannot agree with their interpretation of the results. Their experimental data appear to agree fairly in most cases with the vapour-pressure theory here given, but there are a few notable exceptions. The observed depressions of the freezing-point, for glycerol, $C_3H_5(OH)_3$, given by Jones and Getman* are from three to four times as large as those given by Abegg,† and cannot be fitted by any value of α . The data given by Jones and Bassett‡ for $CaCl_2$ differ considerably from those of Roozeboom,§ and do not agree at all well with the curve in fig. 7B.|| The authors have worked out their results on the assumption of a constant value for the theoretical molecular lowering of the freezing-point, and have obtained widely varying values of the degree of hydration, *e.g.*, from 140 molecules to 12 in the case of glycerine, and 30 to 13 for $CaCl_2$. Their final conclusions, which are diametrically opposed to the theory given in the present paper, are best stated in their own words:

Quotation from Jones and Bassett.¶

"*The Old and the New Hydrate Theory.*—The theory of hydrates in aqueous solutions that we believe to have established by the work, of which this is only a chapter, is to be sharply distinguished from the old hydrate theory of Mendeléeff, which, having long since been shown to be untenable, has been abandoned. According to the older theory, when a substance, like calcium chloride, is dissolved in water, there are formed certain definite chemical compounds, with perfectly definite amounts of water.

"According to the theory established by this work, the compounds formed are, at best, very unstable and vary in combination all the way from 1 molecule of water to a very great number. The composition of the hydrate formed by any given substance is purely a function of the concentration of the solution, or is determined, as we say, by the effect of mass action. Thus the composition of the hydrates formed by calcium chloride may vary all the way from a few molecules of water up to at least 30 molecules, and may have all intermediate compositions, depending solely upon the concentration, temperature being, of course, understood to be constant.

"It is thus obvious that the older and the newer hydrate theories are fundamentally different in character."

Among recent evidence for the existence of hydrates in solution, the

* 'Amer. Chem. Journ.,' vol. 32, p. 320, 1904.

† 'Zeit. Phys. Chem.,' vol. 15, p. 217, 1894.

‡ 'Amer. Chem. Journ.,' vol. 33, p. 546, 1905.

§ 'Zeit. Phys. Chem.,' vol. 4, p. 42, 1889.

|| *Footnote added April 12, 1908.*—One of my students, Mr. W. F. Higgins, working under Mr. S. W. J. Smith's direction, has verified the F. P. depressions in the case of glycerine and calcium chloride. His results agree with those of Abegg and Roozeboom respectively.

¶ 'Amer. Chem. Journ.,' vol. 33, p. 584, 1905.

experiments of Caldwell on the hydrolysis of sugar may be cited.* He attributes the accelerating influence of concentration to the hydration of the sugar molecules, though the degree of hydration cannot be calculated, because the rate of change may be affected by so many other factors. Similarly the degrees of hydration of various salts are estimated by observing the dilution required to reduce the constant K to its normal value. The values thus obtained appear somewhat high, because the possible effects of ionisation are expressly ignored. Whether ions are charged atoms, or whether they are merely unstable hydrates, it seems impossible to ignore their existence. Taking account of the ionisation factor, which is nearly 2 in a solution containing 1 gramme-molecule per litre, the water abstracted by the calcium chloride should be 18 gramme-molecules, according to the freezing-point depression, a result which does not differ greatly from Caldwell's estimate of 22 molecules. The residual difference in this and other cases may well be due to some accelerating influence of the ions as such, which could not be estimated satisfactorily unless allowance were made for the concentrating influence of hydration.

[*Note added March 17, 1908.*—Similar results for the degree of hydration have been deduced by J. C. Philip† from measurements of the solubility of oxygen and hydrogen in various solutions. The degree of hydration found for cane-sugar from Steiner's observations on the solubility of hydrogen was from 5.5 to 6.5 molecules of water to each molecule of sugar, which agrees as nearly as could be expected with the vapour-pressure theory. For salts, not allowing for ionisation, the values obtained for α are higher and more variable than those given by the vapour-pressure theory, *e.g.*, KCl 7 to 11, H_2SO_4 8 to 12, $CaCl_2$ average 21, etc. These values may indicate a specific effect of the solute, apart from mere hydration. Oxygen seems to give different results from hydrogen, *e.g.*, NaCl average $\alpha = 11$ from hydrogen, $\alpha = 14.7$ from oxygen. The method does not appear to succeed so well with more soluble gases or other indifferent substances. It is less simple and direct than the vapour-pressure method, and the effect observed is likely to be more complex.

A large number of data exist for the relative lowering $(p' - p'')/p'$ derived from direct measurements of the vapour-pressure, especially in the case of salt solutions. Very few of these are available for deducing the degree of hydration, either because the ionisation data are deficient, or because the direct measurements of small vapour-pressures are necessarily somewhat

* 'Roy. Soc. Proc.,' A, vol. 78, p. 272.

† 'Faraday Soc. Trans.,' vol. 3, p. 140, 1907.

inexact. But, so far as they go, they appear to be in fair agreement with the vapour-pressure theory.]

General Summary of Conclusions.

21. The foundation of the vapour-pressure theory of solutions here laid down is the assumption of a simple relation between the vapour-pressure and the molecular constitution of the solution. That there should be a simple relation of this kind appears extremely probable when we consider that the concentration of the vapour phase in the solutions here examined is very small, and that such relations generally take a very simple form at extreme dilution. That such a relation should serve as a key to many of the phenomena occurring in solutions is not surprising in view of the fact that equality of vapour-pressure is one of the most general conditions of equilibrium in physical chemistry. The relation of this assumption to the gas-pressure theory, or the hydrate theory, or the capillary-pressure theory, as already indicated, is that it involves them all, since they may be regarded as merely different aspects of the same phenomena. An equivalent assumption may be formulated, at least approximately, in terms of partial pressure, or capillary pressure, or chemical attraction, but it would merely be putting the same thing in different words. The vapour-pressure method appears to be the most direct line of attacking the problem. If, for instance, we regard the changes of capillary pressure in relation to vapour-pressure as defined by the relation $U dP = v dp$, we should arrive at nearly the same result by similar approximations. But this method does not appear to be so convenient, because it involves the volume U , which is generally unknown and variable in an uncertain manner, whereas the volume of the vapour v at low pressures may be regarded as conforming very closely with the laws of gases.

There is no doubt that further experimental work may be required to establish the vapour-pressure theory generally, since accurate data for strong solutions are comparatively scarce. The interpretation of the ionisation factor, and its relation to the heat of dilution, requires further elucidation. Analysis of nearly all the data at present available, in addition to the examples above cited, fails to show any serious disagreement with the vapour-pressure theory. The theory cannot pretend to be exact for all ranges of temperature and concentration, but it seems likely to serve, at least as a second approximation, for co-ordinating results which have hitherto appeared discordant.

Secondary β -rays.

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(Communicated by Professor J. Joly, F.R.S. Received and read March 19, 1908.)

In various papers* published during the last three years I have given an account of work dealing with the emission of secondary β -rays by substances when exposed to the β -rays from radium. The present paper deals with some further points of importance connected with the same subject.

It is not necessary to summarise with any detail the results discussed in previous papers, but the following facts may be briefly mentioned. In these papers no steps were taken to separate the effects due to the primary β radium rays from those produced by the γ -rays that accompanied them; it was sufficiently clear from a few preliminary experiments that the secondary effects due to the γ -rays were very small compared with those produced by the β -rays. As this point has been referred to by other workers† when discussing the results, and as much as 20 per cent. of the total secondary taken as possibly consisting of secondary γ -rays or secondary β -rays due to the γ -rays, I have made some further experiments on the subject.

In the first place, the fraction of the total secondary due to the incident γ -rays was determined by using a magnetic field to deflect the incident β -rays. With the strongest field used the total secondary radiation was cut down to about 4 per cent. of its value when the field was off. This experiment was carried out with the secondary radiation from lead and also from aluminium. The composition of the secondary radiation was then tested by using the magnetic field to deflect it, and it was found to consist almost entirely of β -rays. In both these types of experiments the pencil of rays used and the measuring apparatus employed were taken quite similar to what had been used in the previous work, so that the results I have published in previous papers may be taken as applying to secondary rays, more than 99 per cent. of which are β -rays, and of which 96 per cent. are produced by the

* 'Phil. Mag.,' February, 1905.

'Royal Dublin Society's Trans.'—

"Secondary Radiation," March, 1905.

"Secondary Radiation (Part II) and Atomic Structure," May, 1905.

"The Energy of Secondary Radiation," February, 1906.

"Secondary Radiation from Compounds" (with Mr. Hackett), April, 1906.

"The Absorption of β Radium Rays by Matter" (with Mr. Hackett), March, 1907.

† Kleeman, 'Phil. Mag.,' November, 1907.

incident β radium rays. The same holds for the further results discussed in this paper.

As described in the previous papers, the relative intensity of the secondary radiation has been measured under exactly similar conditions for a large number of elements, and found to depend on the atomic weight of the element, the secondary radiation increasing with the atomic weight, and the rate of increase being such as to divide the elements into divisions corresponding to the chemical periods. The continuous curves (curves D, p. 511), on which the elements are marked without suffix, are taken from a previous paper, and show the relation between the intensity of the secondary radiation and the atomic weight. Further work showed that the rarer elements of the third long period fell into the place reserved for them in this series of curves between iodine and tungsten, the secondary radiation increasing very little with atomic weight in the case of these elements, which fact may be compared with their want of well-defined chemical differences.

The secondary radiation from a large number of compounds was measured and compared with that from the constituent elements, and it was thus shown that the secondary emission of β -particles was strictly an additive atomic property. This result rendered it possible to deduce the secondary radiation for elements usually found in the gaseous form, and for others difficult to obtain pure, and in this way the list of elements shown on curves D was considerably extended, especially as regards the first period, and the third long period, as mentioned above.

It was pointed out that the atomic weight of an element could be determined with considerable accuracy by measuring the secondary radiation from it, especially if it were situated at a place on the curves where the change of radiation is great as atomic weight changes.

No change of secondary radiation could be detected when the temperature was altered, although observations were made with plates raised to very high temperatures.

In further papers the energy of the secondary radiation was compared with that of the primary β -radiation producing it, and in this connection the relative importance of the secondary β -radiation was emphasised, and it was shown how it must be taken into account in studying the passage of β -particles through matter. This subject was developed theoretically and measurements made which gave the true coefficient of absorption of the β -rays, viz., the value the coefficient would have if no secondary particles were produced. This work showed that the ratio of the true coefficient to the density of the absorbing substance depends on the atomic weight of the substance.

Subject of Present Paper.

At the beginning of this work on secondary radiation a few experiments were made on the intensity of the radiation at different inclinations to the normal, and for different angles of incidence, and these few observations indicated that such determinations might give results of importance. They have not, however, been made until now. Comparisons under exactly similar conditions were deemed sufficient for the matters treated in the previous papers, with the exception of the work dealing with the relative energies of the primary and secondary rays, and in that case the conditions were simplified by taking the pencil of primary rays perpendicular to the plate under examination, and measuring for this simple case the intensity of the secondary rays at different inclinations to the normal.

The present paper deals with the intensity of the radiation from the plate in different directions when the incidence rays are not normal. The measurements are carried out with considerable detail in the plane of incidence, and, in addition, measurements are made with another form of apparatus designed to give the total secondary radiation in all directions from the plate for different angles of incidence of the primary rays. One important result of these detailed observations may here be indicated in a few words. A portion of the secondary β -rays follows approximately the ordinary law of reflexion. This portion is not very different in amount, no matter what the plate exposed to the primary radiation consists of. The nature of this portion of the secondary radiation is discussed later; for convenience we shall refer to it in future as the "reflected" portion. When the secondary radiation is measured in such a way as to be comparatively free from reflected rays, it depends on the atomic weight of the substance in an even more striking manner than that shown in the previous work, where the method of measurement was such as to include some reflected rays.

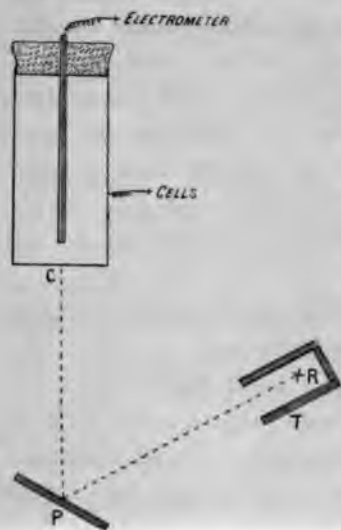
Apparatus.

The apparatus used in the first part of the paper was very simple and similar to that employed in the previous experiments.

P represents the material emitting the secondary rays; it is in the form of a circular plate 7.5 cm. diameter, and is exposed to the β -rays from the radium R. P is thick enough to prevent the transmission of β -rays, and thus gives the maximum amount of secondary rays. The radium is enclosed in a short lead tube T which limits, to some extent, the β -rays to a

cylindrical pencil, but the actual intensity of the pencil of rays falling on P, when the angle of incidence is changed, is determined by direct experiment, as described later.

C is a cylindrical vessel 20 cm. long and 7.5 cm. diameter, with a thick wire stretched along its axis and joined to an electrometer, the cylinder being kept connected to cells and the current to the central terminal measured in the usual way. The end of the cylinder through which the secondary rays enter is covered with a single sheet of tinfoil. The distances CP and RP are each 20 cm.



The tube T and the plate P are both movable, the former around a horizontal circle with P as centre, and the latter about a vertical diameter. When both are turned through the same angle, the angle of incidence remains constant, and measurements of the secondary rays at different angles in the plane of incidence are thus obtained. Such measurements are taken for various angles of incidence.

The plate P can easily be removed and

replaced, so that an observation can be taken without the plate, giving the current in C due to unscreened direct radiation from R and other causes, and then another with the plate replaced, the increase being due to the secondary rays from the plate.

In practice it was found inconvenient to screen off the direct rays to a sufficient extent and at the same time retain the necessary freedom of motion of T. The difficulty was met by joining a second ionisation tube like C to the electrometer, and exposing it to a separate small quantity of radium, this second tube being joined to give a charge to the electrometer opposite in sign to that from C. The position of the radium acting on this second tube could easily be adjusted to almost compensate the unscreened radiation from R, and thus enable a sufficiently small capacity to be used with the electrometer.

The amount of primary radiation falling on the plate P is not constant when the angle of incidence θ changes, and to reduce the observations to a common basis it is necessary to know the relative amounts for different values of θ . This was found by placing the tube T directly facing the cylinder C at a distance from it equal to PR, and measuring the ionisation produced in C when the end facing the radium was covered in succession by a

series of thick lead plates pierced with apertures proportional in area to the different values of $\cos \theta$.

It might appear that the comparison thus found would not be accurate, as rays entering through a small area near the centre might not produce the same ionisation as the same rays entering farther from the centre. The error thus introduced was, however, shown to be small, by moving a plate with a small opening in it so as to bring the opening to different positions on the end of the cylinder.

Results of Experiments.

The secondary radiation has been fully studied in the plane of incidence as described above for the elements lead, tin, copper, and aluminium. The primary exciting β -rays are allowed to fall on the exposed plate at a certain angle, and this angle is kept constant, while the intensity of the secondary rays is measured at various angles to the normal, and a curve plotted. The angle of incidence is then altered, and another curve plotted. This has been done for angles of incidence of 0° , 30° , 45° , 60° , and 75° . The curves for the different angles of incidence are then reduced so as to correspond to equal amounts of primary rays impinging on the plate. The numbers required for this reduction are given below, and were determined as has been described.

| Angle of incidence θ . | Amount of primary rays impinging on plate. |
|-------------------------------|---|
| 0° | 100 |
| 30° | 96 |
| 45° | 79 |
| 60° | 62 |
| 75° | 34 |

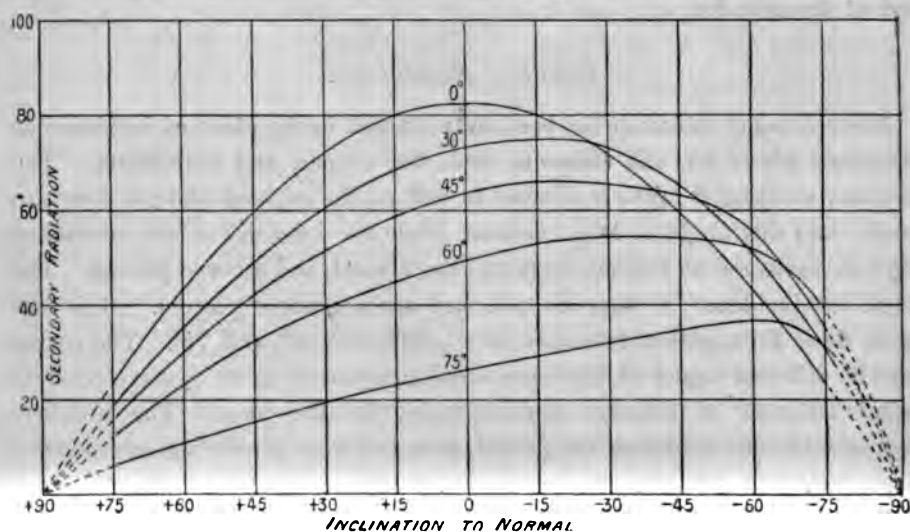
The observations with lead are shown by the curves A. The number on each curve is the angle of incidence of the primary rays, which is constant for all points of the curve. The secondary radiation is plotted for different angles of emission; angles on the same side of the normal as the incident primary rays are marked with a plus sign, and angles on the opposite side with a minus sign. Observations were made at different angles varying from $+75^\circ$ to -75° .

Curves B are calculated from Curves A and the numbers given above, so that the curves for different angles of incidence of the primary rays now correspond to equal amounts of primary rays impinging on the plate.

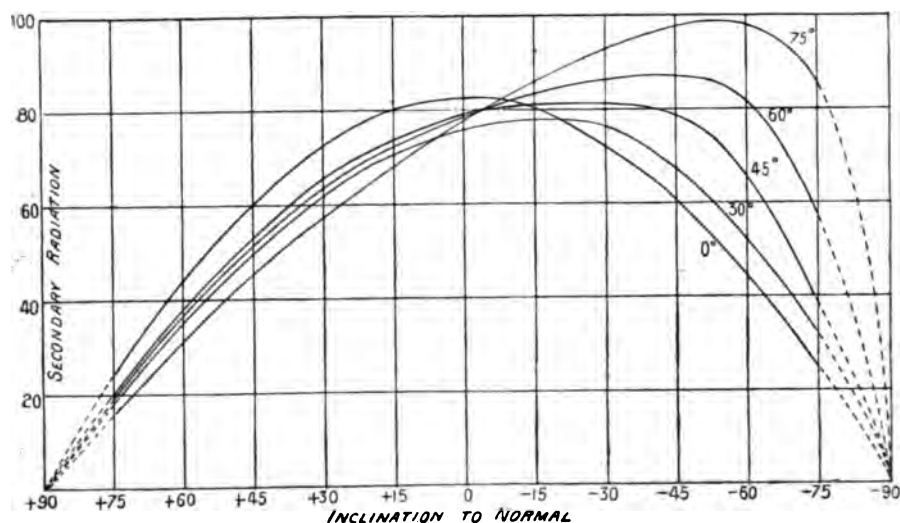
Curves A_1 and B_1 are the similar curves for tin, and curves A_2 and B_2 for

aluminium. The different curves for the same element, and the curves for the various elements, are all plotted to the same scale.

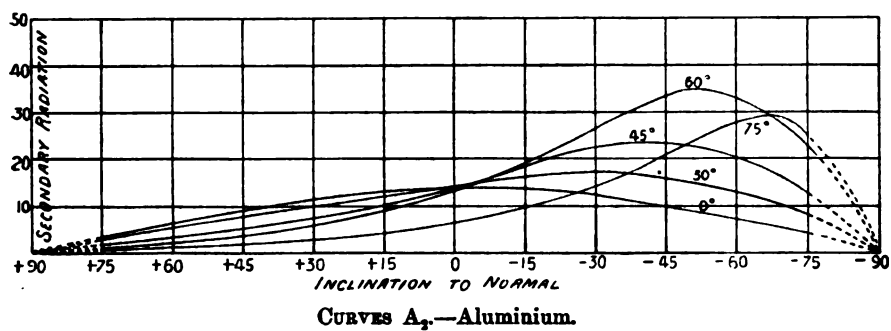
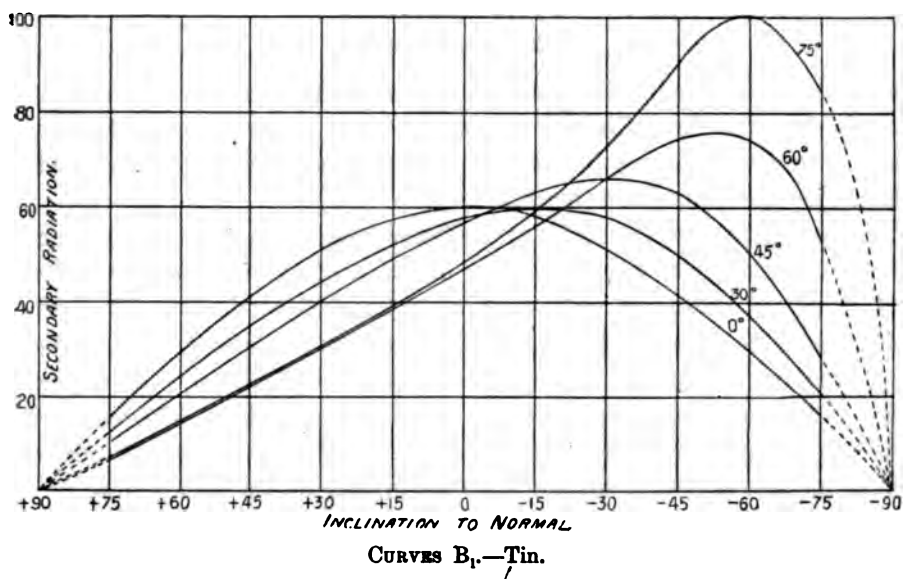
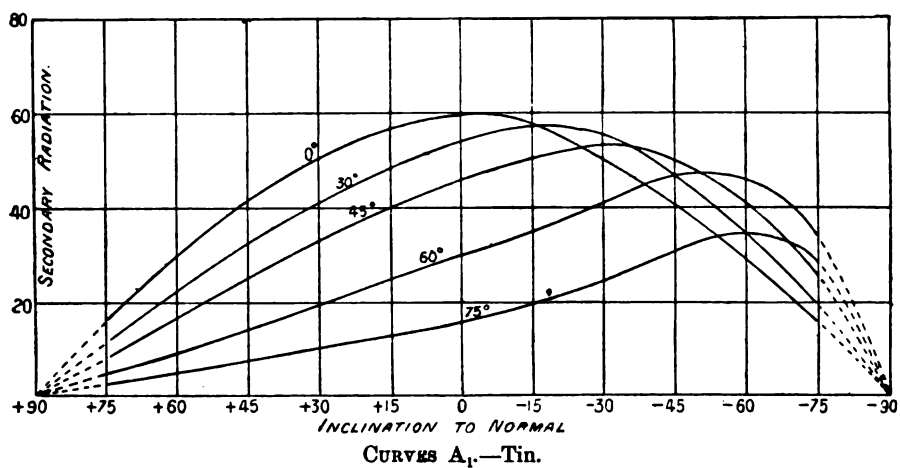
Before describing other experimental results, some of the features of these curves may be briefly referred to. The curve for normal incidence, which is, of course, symmetrical on the plus and minus sides, is almost exactly a cosine curve, showing that when the primary rays are normal to the exposed plate the secondary radiation in any direction is proportional to the cosine of the

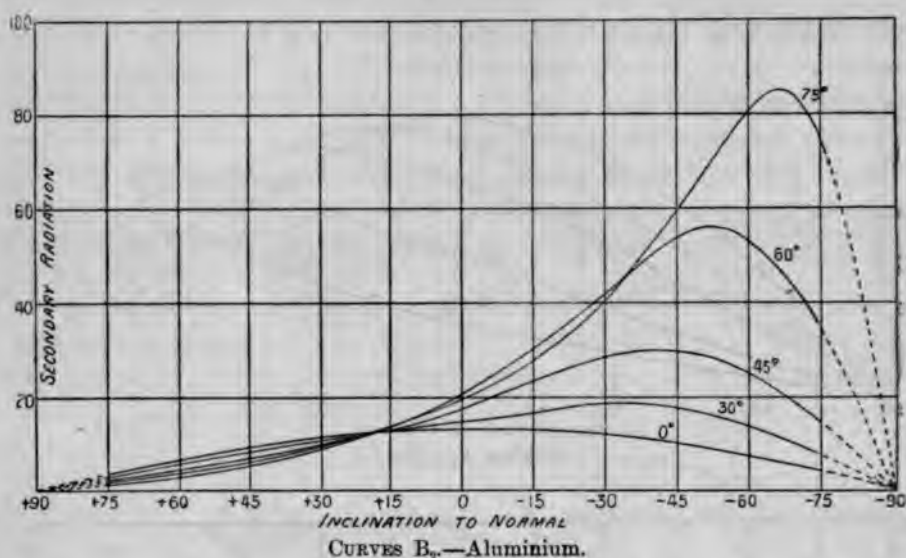


CURVES A.—Lead.



CURVES B.—Lead.





angle between that direction and the normal. This result should follow from the fact that the radiation from an element of volume at a depth in the plate traverses a thickness inversely proportional to the cosine of the angle between its direction and the normal.

The curves for other than normal incidence have a maximum ordinate on the side of the normal away from the direction of the incident rays. The position of the maximum ordinate is more inclined to the normal as the incident rays are more inclined. In fact, the form of the curves suggests that the secondary radiation is made up of two parts, one of which is of importance in directions near to the direction of ordinary reflexion. This reflected portion is evidently a greater fraction of the total secondary in the case of aluminium than in that of tin, and similarly greater for tin than for lead.

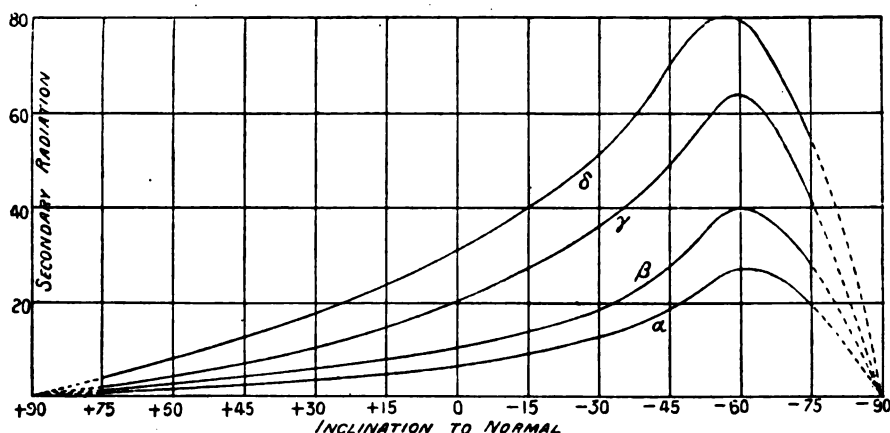
Curves for copper were also plotted, but for economy of space are not reproduced; they were in every sense intermediate in character to those for tin and aluminium. All the results, therefore, agree in showing that the portion of the secondary radiation which we refer to as reflected rays is of greater relative importance the smaller the atomic weight of the substance. This follows, not because the reflected radiation is actually greater for low atomic weights, but because the other portion of the secondary radiation—the true secondary—diminishes rapidly with the atomic weight.

A rough method of analysing the curves is to take the difference between the ordinates for equal angles on the plus and minus sides, and to regard this difference as representing the reflected portion of the secondary radiation. When this is done the position of the maximum of the reflected rays agrees

very closely with the position of ordinary reflexion, and the magnitude of the reflected portion for any angle of incidence does not vary very much for the different elements tested.

The Effect at the Surface of the Plate.

To test the effect at the surface of the plate, experiments were carried out with layers of aluminium. Curves C show the results, the separate curves α , β , γ , δ being for thicknesses of 0.0027 cm., 0.0052 cm., 0.0208 cm., and a large number of layers almost thick enough to give the maximum secondary radiation. The angle of incidence of the primary rays is 60° for each of the



CURVES C.

curves, so that the reflected portion is an important part of the whole. The curves are not plotted to scale with those for aluminium given above. An analysis of these curves shows that the reflexion is not merely a surface action, but, as might be expected, it goes on at successive layers beneath the surface. The reflected portion, however, increases less rapidly than the total radiation when the thickness of the plate is increased.

Absorption of Secondary Rays.

A few experiments were made on the rate of absorption of the secondary rays: (1) when the primary rays fell normally on the plate and the secondary rays were observed in a direction as near the normal as convenient—about 15° from it; (2) when the angle of incidence was 60° , and the direction of the secondary rays also 60° from normal. In case (1) the radiation should consist almost entirely of true secondary according to the view we have been taking, and in case (2) the reflected portion should be important.

In previous papers the observations required to obtain an accurate value of the coefficient of absorption of rays producing secondary rays were explained; but as for our present purpose we only require approximate relative results, measurements of the ordinary simple type were made. The intensity of the secondary rays was measured before and after passing through an absorbing layer of three sheets of tinfoil. The ratio of the second intensity to the first is given in the following table:—

| Substance emitting the secondary rays. | Ratio of intensities. | |
|--|--|---|
| | Incident rays normal. Secondary rays 15° to normal. | Incident rays + 60° to normal. Secondary rays - 60° to normal. |
| Pb | 0·63 | 0·74 |
| Pt | 0·63 | 0·74 |
| Sn | 0·60 | — |
| Ag | 0·59 | — |
| Cu | 0·57 | 0·74 |
| Al | 0·50 | 0·70 |

The corresponding ratio for the primary β radium rays is 0·75.

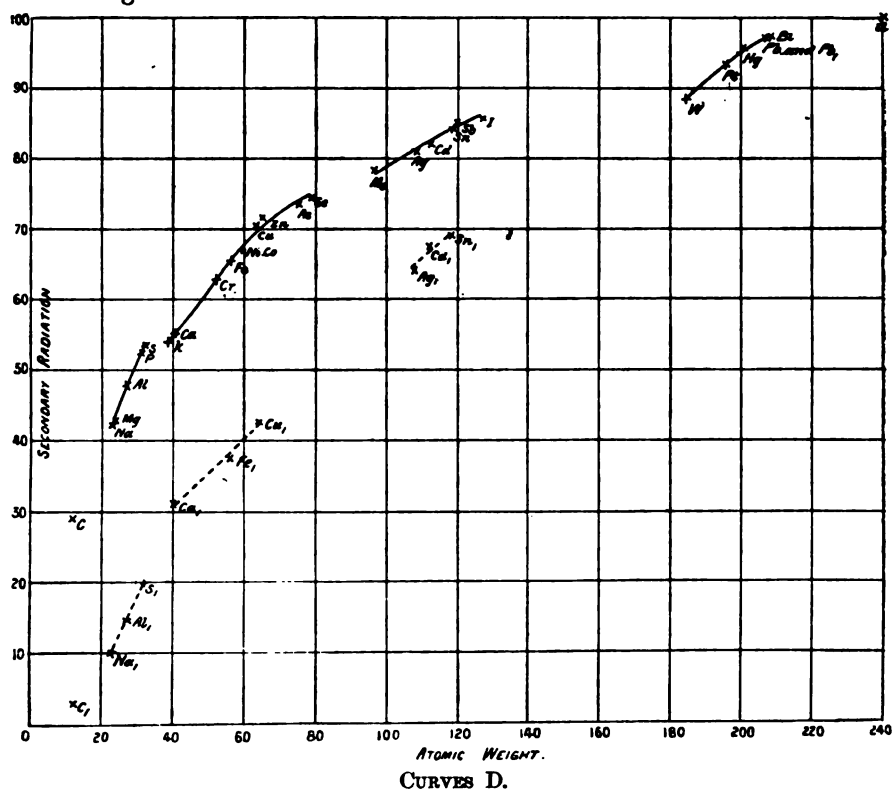
These rough determinations show clearly enough that there is good ground for dividing the total secondary radiation into two distinct parts. When the incident rays are normal, and, therefore, the reflected part small, the rate of absorption of the secondary rays from different substances is decidedly different, and in all cases is greater than that of the primary rays. On the other hand, when the conditions are favourable for greater reflexion, the angles of incidence of primary and emission of secondary being large and equal, the rate of absorption varies much less from one substance to another, and is in all cases not very different from that of the primary rays. A complete investigation of the absorption of the secondary rays from a large number of substances would obviously be of great importance. An interesting connection between the absorption and the atomic weight of the substance emitting the rays would no doubt be found.

Secondary Radiation and Atomic Weight.

The relation between the intensity of the secondary radiation from an element and its atomic weight has already been described.

The results of previous work are represented by the curves D (continuous part). In these experiments care was taken to place the different elements examined in exactly the same position relative to the incident rays, but this position was such as to give a considerable proportion of what we now call reflected rays. In addition to the experiments with lead, tin, copper, and

aluminium, described above, observations have been made with a few other elements, so as to indicate more fully the new form of these curves connecting secondary radiation and atomic weight when the incident rays fall normally on the exposed plate and the secondary radiation is measured in a direction near the normal; 15° from the normal was taken, as, with the apparatus used, it was inconvenient to make direct measurements for a smaller angle.



The results are shown by the discontinuous curves D, on which the elements are marked with a suffix. The scale used in plotting these curves is such as to make the position of lead coincide with its position on the other curves.

The connection between the secondary radiation and the atomic weight is brought out in an even more striking manner by these later curves, and the divisions corresponding to the chemical periods previously pointed out are quite clear. It would be important to make a fresh examination of a more complete list of elements in the light of the further knowledge regarding the secondary rays that we now possess.

Part II.—MEASUREMENTS OF THE TOTAL SECONDARY RADIATION IN ALL DIRECTIONS FOR DIFFERENT ANGLES OF INCIDENCE.

Apparatus.

The work described in the first part of this paper is confined to measurements of the secondary radiation in the plane of incidence. To complete the work, similar observations should be carried out in planes other than that of incidence. This has not, however, been done as yet, chiefly on account of the time necessary, but the total secondary radiation has been measured directly.

A form of apparatus was used which gave directly the total radiation in all directions from the exposed plate for different angles of incidence of the primary rays. An ionisation vessel was constructed, consisting of three concentric hemispheres, of radius 20, 25, and 30 cm. respectively, the hemispheres being made of a framework of a few wires, and covered with a single layer of tinfoil. The inner and outer hemispheres rested on a wooden base covered with tinfoil, the two hemispheres and the base being joined to cells and kept at a high potential. The middle hemisphere was insulated from the others and joined to an electrometer, and the ionisation current between the middle and the other hemispheres measured in the usual way. A circular opening at the centre of the base of the hemispheres allowed a plate of the material under examination to be brought into position in the plane of the base from below and removed at will. A narrow opening in the three hemispheres along a meridian allowed a lead tube containing radium to project just inside the inner hemisphere, so that a pencil of β -rays fell on the central portion of the base, including the plate exposed in the circular opening. The difference between the electrometer readings when the plate was in position and when it was removed gave the ionisation due to the secondary radiation from the plate. The tube containing the radium could be moved along the meridian so as to vary the angle of incidence on the exposed plate.

The ionisation vessel, consisting of the space between the middle and the inner and outer hemispheres, being symmetrical with respect to the exposed plate, and thus giving the same path length to all secondary rays, the rates of charging of the inner hemisphere were approximately proportional to the total secondary radiation, irrespective of the distribution of this radiation. Effects due to tertiary and radiations of a higher order might introduce some error, as the symmetry would not hold for such rays.

With this apparatus the conductivity between the hemispheres, due to unscreened direct rays, was necessarily great, but this difficulty was met,

as in the experiments with the former apparatus, by a compensating arrangement. In the present case the current required for approximate compensation was fed into the electrometer by a number of small storage cells acting through a very large variable resistance. Steady results could easily be obtained, as with this apparatus and the quantity of radium used the secondary radiation from plates of 7.5 cm. diameter was large enough to allow the use of a capacity of 0.5 microfarad joined to the electrometer.

Results of Experiments.

The total secondary radiation has been measured in this way for lead, tin, copper, and aluminium for angles of incidence of the primary rays ranging from 10° from normal to 80° from normal.

As in the work described in the first part of the paper, the amount of primary radiation impinging on the plate varies with the angle of incidence, and the relative amounts at different angles were determined as before. These relative amounts are given below; they are very similar to the corresponding numbers in the first part of the paper, as the pencils of β -rays used were very similar in the two cases.

| Angle of incidence. | Amount of primary radiation impinging on plate. |
|---------------------|--|
| 0° | 100 |
| 10° | 99 |
| 30° | 93 |
| 45° | 82 |
| 60° | 60 |
| 75° | 33 |
| 80° | 23 |

The total radiations for the four elements tested are given in the following tables. In Table A the observed numbers are given on an

Table A.

| Angle of incidence of primary rays. | Total secondary radiation. | | | |
|--|----------------------------|-----|-----|-----|
| | Pb. | Sn. | Cu. | Al. |
| ° | | | | |
| 10 | 58 | 38 | 24 | 9 |
| 30 | 56 | 37 | 26 | 10 |
| 45 | 50 | 36 | 25 | 12 |
| 60 | 41 | 34 | 25 | 14 |
| 75 | 19 | 15 | 15 | 9 |
| 80 | 13 | 9.5 | 6.5 | 4 |

arbitrary scale, and in Table B these numbers are reduced so as to correspond to equal amounts of primary rays at the various angles, the reduction being made by means of the numbers given above.

Table B.

| Angle of incidence of primary rays. | Total secondary radiation for equal amounts of primary rays. | | | |
|--|--|-----|-----|-----|
| | Pb. | Sn. | Cu. | Al. |
| ° | | | | |
| 10 | 58 | 38 | 24 | 9 |
| 30 | 60 | 40 | 28 | 11 |
| 45 | 61 | 44 | 30 | 15 |
| 60 | 68 | 57 | 42 | 23 |
| 75 | 58 | 46 | 46 | 27 |
| 80 | 56 | 41 | 28 | 17 |

A comparison of these numbers, showing the total secondary radiation corresponding to various angles of incidence, with those previously given, showing the secondary radiation in the plane of incidence, enables us to draw some inferences regarding the radiation in planes other than that of incidence. From the way in which the total radiation varies, especially in the case of the elements of lower atomic weight, we see that the "reflected" rays are an important factor of the whole, and are not confined to the plane of incidence. The relative decrease of the total radiation for very large angles of incidence probably means that for such angles the "reflected" radiation is more confined to the plane of incidence than for smaller angles.

Nature of the Secondary β -rays.

The experimental work described in this paper affords strong evidence that the secondary β -rays may usefully be looked upon as consisting of two parts: the true secondary rays, and the "reflected" rays. These two parts differ essentially as regards distribution, they differ somewhat in character, and they probably differ also in origin. The difference in distribution and the variation of the distribution with the angle of incidence of the primary rays have been described at sufficient length, and the difference in character is shown by the measurements on absorption described above.

It is important to consider what difference there may be in the origin of these two parts of the secondary rays.

There is considerable evidence in favour of regarding the reflected rays as consisting of some of the incident β -particles, which, in the path they have

traversed in the exposed plate, have not actually penetrated into or at least not caused any change of energy of any atomic system. Such a particle should leave the plate with its initial velocity unaltered in magnitude. Its velocity parallel to the surface of the plate should also be unaltered, as the resultant forces acting on it should be normal to the plate. Its direction of emergence should therefore be inclined to the normal at an angle equal to that of incidence. These conditions might well be satisfied with sufficient accuracy to explain the observed maximum of reflected rays in the direction corresponding to that of ordinary reflexion.

The other portion of the secondary radiation, called in this paper the true secondary, has been discussed at some length in the previous work referred to at the beginning of this paper. The remarkable relation between the intensity of this radiation and the atomic weight of the substance emitting it was taken as strong evidence that the β -particles composing it were particles expelled from the atoms when disturbed by the entry of the primary rays. If these secondary particles were merely scattered primary particles, it is difficult to see how such a relation between the intensity and the atomic weight could possibly arise. If they are particles expelled from the atom, such a relation would easily admit of explanation.

Whether the expelled particles are original constituents of the atom, or incident particles absorbed by the atom and subsequently expelled, does not really amount to any essential difference. It is true that from the latter point of view we might, in a sense, regard the secondary particles as scattered primary particles, but scattering in this special sense would, as just stated, be practically identical with the explanation advanced in this and the previous papers.

On Scandium.

By Sir WILLIAM CROOKES, D.Sc., F.R.S.

(Received March 4,—Read April 30, 1908.)

(Abstract.)

Scandia is one of the rarest and least known of the recognised rare earths. It was discovered in 1879 by Nilson, who separated it, together with ytterbia, from erbia extracted from euxenite and gadolinite. Later in the same year Cleve extracted scandia from gadolinite, yttrotitanite, and keilhauite, and described the scandium sulphate, double sulphates, nitrate, oxalate, double oxalates, selenate, acetate, formate, oxide, and hydrate, and gave some of the chief reactions of the new body.

In the course of my 20 years' work on the fractionation of the rare earths I have repeatedly tested my products by examining their photographed spectra, using the dominant lines of the various elements as tests for their presence. Scandium has an extremely characteristic group of lines in its spectrum, situated between wave-lengths 3535·864 and 3651·983, the strongest being at 3613·984, midway between two strong iron lines. By using a part of the spectrum in which this occupies the centre of the photograph it is easy to see if scandium is present. Detecting the dominant line, the presence of scandium can be verified by reference to the other lines of the group.

Scandium I found in some of my fractions, but only in small quantities. A few years ago I commenced an examination of all the obtainable rare earth minerals, in order to see if any of them showed more than a trace of scandium. The minerals examined were:—

| | | |
|------------------------|--------------------------|-----------------------------------|
| Æschynite. | Homolite. | Thalenite. |
| Allanite. | Keilhauite. | Thorianite. |
| Alvite. | Knopite. | Thorite. |
| Auerlite. | Koppite. | Thorogummite. |
| Baddeleite (Ceylon). | Lanthanite. | Tscheffkinita. |
| Bastnasite. | Monazite. | Tysonite. |
| Broggerite. | Mosandrite. | Urdite. |
| Cerite. | Orangite. | Wiikite. |
| Clevite. | Orthite. | Xenotime. |
| Columbite. | Polycrase. | Yttergarnet. |
| Cryptolite. | Pyrochlore. | Yttrialite. |
| Eudialite. | Rhabdophane. | Yttrocerite. |
| Euxenite. | Samarskite. | Yttrugummite. |
| Fergusonite (Ceylon). | Scheelite (Bohemia). | Yttrotantalite. |
| Fergusonite (Ytterby). | Scheelite (New Zealand). | Yttrotitanite. |
| Fluocerite. | Schorlomite. | Zirkelite (Ceylon, sp. gr. 5·0). |
| Gadolinite. | Sipylite. | Zirkelite (Ceylon, sp. gr. 4·42). |
| Hielmite. | Tantalite. | |

Of the minerals examined, scandium was detected in auerlite, cerite, keilhauite, mosandrite, orangite, orthite, pyrochlore, thorianite, thorite, and wiikite, but while other minerals contained less than 0·01 per cent. of scandium, wiikite was found to contain more than one hundred times that amount.

Wiikite is a black amorphous mineral of specific gravity 4·85. Its hardness is 6. It is infusible before the blowpipe. It is imperfectly attacked by strong mineral acids, and breaks up easily when fused with potassium bisulphate. Heated to full redness in a silica tube, it gives off helium, water, and a distinct amount of sulphuretted hydrogen, followed by a white sublimate. The mineral begins to crack at a temperature a little below redness, and at the approach of redness gas is evolved with almost explosive violence, the mineral breaking up and flying about the tube. A fragment so treated examined under the microscope shows the surface covered with glistening points. With a high power these points are resolved into a mass of minute cubes, curiously regular in form and appearance. Heating drives off 5·83 per cent. of its weight; 5·82 of the loss is water and acid vapour, the difference, 0·01 per cent., consisting chiefly of helium, with a little hydrogen, carbon dioxide, and a mere trace of neon.

Containing so many bodies, the exact separation of which one from the other is not known, it is at present impossible to give an accurate and complete analysis of wiikite. The following is considered to be a fair approximation to its composition:—

| | |
|---|--------|
| Tantallic acid with some niobic acid | 15·91 |
| Titanic acid and zirconia..... | 23·36 |
| Earths of the cerium group | 2·55 |
| Earths of the yttrium group | 7·64 |
| Scandia..... | 1·17 |
| Thoria | 5·51 |
| Ferrous oxide | 15·52 |
| Uranic oxide | 3·56 |
| Silica | 16·98 |
| Water and gases | 5·83 |
| Calcium, manganese, tin, sulphur, etc., unestimated | 1·97 |
| | <hr/> |
| | 100·00 |

After the crude earths, chiefly yttria, ytterbia, and scandia, have been separated from the mineral, they are "fractionated" by methods described in the paper. Towards the end of the fractionation the chief impurity is

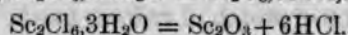
ytterbium. Fortunately the very strong dominant line of the ytterbium spectrum, wave-length 3694·344, occurs at a vacant part of the scandium spectrum, and near the characteristic group of scandium. A sample of scandia is not taken as satisfactory if the least trace of this line is seen on an over-exposed spectrum of scandium, and if the atomic weight is higher than 44·1. The atomic weight of ytterbium being 173, a very little of it as an impurity raises the atomic weight of scandium.

I have prepared and analysed the following compounds of scandium :—

Scandium hydroxide, $\text{Sc}_2\text{O}_3 \cdot 3\text{H}_2\text{O} = \text{Sc}(\text{OH})_3$.

Scandium carbonate, $\text{Sc}_2(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$.

Hydrated scandium chlorides, $\text{Sc}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O} = \text{Sc}_2\text{O}_3 \cdot 6\text{HCl} \cdot 9\text{H}_2\text{O}$,



Hydrated scandium bromides, $\text{Sc}_2\text{Br}_6 \cdot 12\text{H}_2\text{O}$, $\text{Sc}_2\text{Br}_6 \cdot 3\text{H}_2\text{O} = \text{Sc}_2\text{O}_3 \cdot 6\text{HBr}$.

Scandium chlorate.

Scandium perchlorate.

Scandium bromate.

Scandium sulphates, $\text{Sc}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sc}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$.

Anhydrous scandium sulphate, $\text{Sc}_2(\text{SO}_4)_3$.

Basic scandium sulphate, $\text{Sc}_2\text{O}(\text{SO}_4)_2$.

Scandium and potassium double sulphate, $3\text{K}_2\text{SO}_4 \cdot \text{Sc}_2(\text{SO}_4)_3$.

Scandium selenates, $\text{Sc}_2(\text{SeO}_4)_3 \cdot 8\text{H}_2\text{O}$, $\text{Sc}_2(\text{SeO}_4)_3 \cdot 2\text{H}_2\text{O}$.

Scandium nitrates, $\text{Sc}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$, $\text{Sc}(\text{NO}_3)_3$, $\text{ScOH}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Sc}_2\text{O}(\text{NO}_3)_4$.

Scandium formate, $(\text{HCOO})_2\text{ScOH} \cdot \text{H}_2\text{O}$.

Scandium acetate, $(\text{CH}_3\text{COO})_2\text{ScOH} \cdot 2\text{H}_2\text{O}$.

Scandium propionate, $(\text{C}_2\text{H}_5\text{COO})_2\text{ScOH}$.

Scandium butyrate, $(\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COO})_2\text{ScHO}$.

Scandium iso-butyrate, $\left(\begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix} > \text{CH} \cdot \text{COO}\right)_2\text{ScOH} \cdot 2\text{H}_2\text{O}$.

Scandium iso-valerate, $(\text{C}_4\text{H}_9\text{COO})_2\text{ScOH} \cdot 2\text{H}_2\text{O}$.

Scandium oxalates, $\text{Sc}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$, $\text{Sc}_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$, $\text{Sc}_2(\text{C}_2\text{O}_4)_3 \cdot 2\text{H}_2\text{O}$,
 $\text{Sc}_2(\text{C}_2\text{O}_4)_3 \cdot \text{H}_2\text{O}$.

Scandium picrates, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}]_2\text{ScOH} \cdot 14\text{H}_2\text{O}$,
 $[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}]_2\text{ScOH} \cdot 5\text{H}_2\text{O}$.

Scandium pyromellitate.

Scandium camphorate.

*Note on the Trajectories of Rifled Projectiles with
Various Shapes of Head.*

BY A. MALLOCK, F.R.S.

(Received February 24,—Read March 19, 1908.)

In two previous papers* I gave an approximate formula for the determination of the range and elevation of a pointed rifle projectile, of which the head was an ogive with a radius of two diameters. This approximation agreed so closely with the results obtained in practice that it seemed worth while to ascertain whether the same type of formula would not apply equally well to other shapes of head. For this purpose I have made the

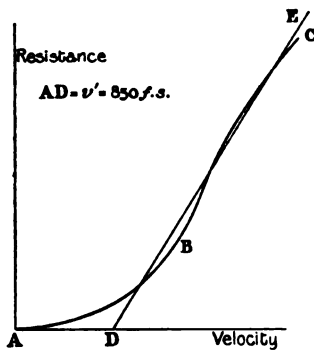


DIAGRAM I.

experiments which will be presently described. In order to explain clearly what the exact points to be decided were, I will briefly restate the origin of the formulæ given in the former papers.

The results of all the experiments made on air resistance at high velocities agree in giving a curve of retardation in terms of velocity of the form shown in Diagram I.

The assumption made in the approximate formula for the range is, that, for practical purposes, the curve ABC may be replaced by the straight line DE, as far as retardation R between the velocities of 1000 and 3000 f.s. is concerned.

This leads, as was shown, to the following expressions for the remaining velocity v , and the distance s travelled in a given time,

$$v = v' + u_0 e^{-at}, \quad (1)$$

$$s = v't + \frac{u_0}{a}(1 - e^{-at}). \quad (2)$$

The quantity a is the coefficient of $v - v'$ in the equation to the straight line CD, viz.:—

$$R = a(v - v') = au.$$

It was further found, from the analysis of a large quantity of range practice, that the downward acceleration of the shot during its flight was less than the acceleration due to gravity, that is to say, the air resistance

* 'Roy. Soc. Proc.' A, vol. 79, pp. 274 and 576.

produced an upward force, as well as a retardation in the direction of motion, and that the effective downward acceleration (g') could be expressed as a function of the reduction of velocity. Thus instead of taking the fall in time t as $\frac{1}{2}gt^2$, the results showed that we should write $g - gc(1 - e^{-at})$ for g . The numerical value of c for the class of projectiles considered was about 0.265.

This change in the downward acceleration implies that the axis of the projectile is slightly inclined to the trajectory, and that the angle between the two increases as the velocity decreases, that is, as the curvature of the trajectory increases; and this is what might naturally be expected to happen.

Using the above value for g' , the angle of elevation α , with which the projectile must start, if it is to remain in the air for the time t , is given by $\alpha = \frac{1}{2} \frac{gt^2}{s} v - c(1 - e^{-at})$.

For brevity, I will write x for at , and z for $1 - e^{-at}$, which gives

$$\alpha = \frac{x^2(1 - cz)}{2a(v'x + u_0z)}. \quad (3)$$

It will be noticed that in this expression for α there are three constants, v' , c , and a . Of these, v' and c are purely experimental. The constant a , however, can be decomposed into factors, one of which is experimental, while the other depends on the size, weight, and density of the projectile.

The object of the present series of experiments was in the first place to find out whether values could be assigned to v' , c , and a , which would make the formulæ (1), (2), and (3) agree with observation for different shapes of head, and, secondly, in what manner these constants changed with the shape.

The shapes employed for the head of the experimental projectiles were:—

- (1) Flat heads.
- (2) Hemispherical heads.
- (3) Ogival heads, radius of ogive 2 diameters.
- (4) " " " 4 "
- (5) " " " 6 "
- (6) " " " 12 "

All these projectiles were made of brass, 0.303 inch diameter and weighing 154 grains (10 grammes nearly). They were fired with a muzzle velocity of 2480 f.s. and their trajectories were determined by practice up to a range of 1000 yards. It was found, in every case, except with the flat heads, that values could be found for v' , c , and a , which would make the formula represent the facts within the limits of errors of observation and, further, that v' and c were apparently independent of the shape of the head.

The chief interest therefore attaches to the dependence of a on the shape of the head. The quantity represented by a first occurs as the coefficient of u in the equation of the straight line, which is taken to represent the retardation due to air resistance; and since, then, $a \times$ a velocity is equal to a retardation, the dimensions of a are T^{-1} .

Again, a appears as the coefficient of t in the expression for the remaining velocity, viz., $v = v' + u_0 e^{-at}$. Hence a is the reciprocal of the time in which the velocity u (or $v - v'$) is reduced by the air resistance in the ratio of e to 1.

And again, the retardation of the projectile is equal to mean air pressure (P) per unit area of cross-section of the projectile \times that area \div the mass: or

$$au = \frac{\pi P d^2}{4M}, \quad \text{so that} \quad a = \frac{P}{u} \frac{\pi g d^2}{4W}.$$

The formulæ (1), (2), (3) assume that P/u is a constant depending on the shape of the head of the projectile only.

To determine this constant it is only necessary to determine the a for each shape of head from the data furnished by practice at various ranges. This may be done as follows:—

Let α_n be the angle of elevation found by experiment as giving a range of s feet to a projectile having an ogival head of n diameters radius. We have

$$s = \frac{1}{\alpha_n} (v'x + u_0 z) \quad \text{and} \quad \alpha_n = \frac{g't^2}{2s} = \frac{g'x^2}{2\alpha_n^2 s}, \quad (4)$$

whence, eliminating α_n , we have

$$x = u_0 z / \left(\sqrt{\frac{g's}{2\alpha_n}} - v' \right). \quad (5)$$

By plotting the function on the right hand in terms of x , the value of x which fulfils the conditions of (5) can be found, and substituting this value in (4) we find α_n . A comparison can then be made between the trajectory found by experiment and that given by the formulæ (1), (2), (3).

I will not add to the length of this paper by giving the somewhat tedious computations required, but the results are shown in Diagrams (II), (III).

Diagram II gives the observed angles of elevation required at 1000 yards for the various bullets tried, plotted in terms of the radius of the ogive expressed in diameters of the projectile.

Diagram III shows the value which must be assigned to a if a shot fired with velocity 2000, 2200, etc., f.s. requires an angle of elevation α for 1000 yards.

By putting $\alpha = 0$ we find the minimum angle of elevation which a projectile at the given range can have, and the values so found approach the angles actually used with large projectiles at ranges short enough to make the reduction of velocity by air resistance inconsiderable.

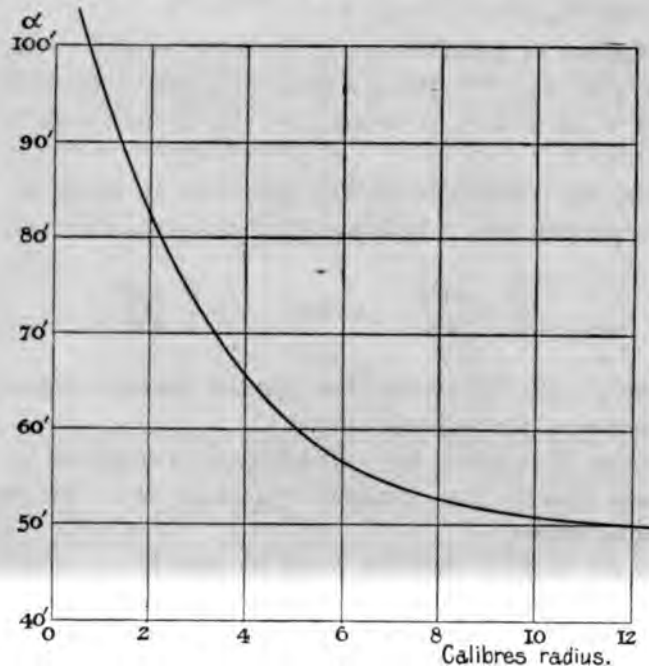


DIAGRAM II.—Angle of elevation found by experiment for ogival-headed projectiles in terms of the radius of the head.

Weight of projectile, 154 grains. Muzzle velocity, 2480 f.s.

In Diagram IV the full curves represent the angles of elevation for various ranges, computed from the calculated value of α_1 , and the spots refer to the observed values. It will be seen that the agreement between the calculated and observed results is fairly close.

Diagram V gives the calculated values of P/u for the different shapes of head employed.

In order to test the formula at a different muzzle velocity, a series was fired with a bullet made commercially, which has nearly the same form, weight, and density as the 12-diameter ogive experimental bullet, but having a muzzle velocity of 2880 feet per second. The result is shown in Diagram VI, Curve A. Here the experimental result is in very close agreement with the calculation.

The Curve B in the same diagram refers to a bullet of the same weight,

density, muzzle velocity, and the same external shape, except that the point is removed, leaving a flattish area about 0.05 inch diameter. In this case and in that of the Curve C_1 , which refer to a bullet weighing 225 grains, having

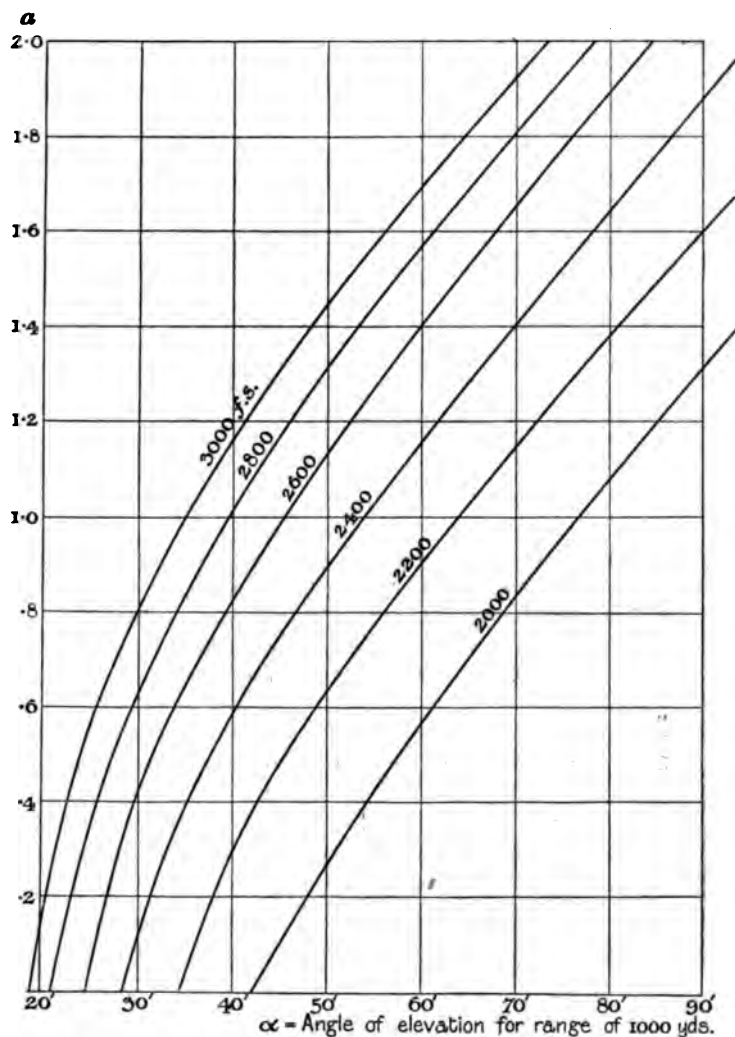


DIAGRAM III.—Showing the values of “ a ” for an ogival-headed projectile in terms of the angle of elevation “ a ” required for a range of 1000 yards, and with muzzle velocities of from 2000 to 3000 f.s.

the same shape of head as B, and the same flattened point, but with a greater density (muzzle velocity 2225 f.s.) the difference between the calculated and experimental curves is considerable. But with values of a used in Curves B and C_3 the agreement with the formulæ again becomes very close.

(The constant difference between C_3 and C_2 is probably due to a zero error in sighting.)*

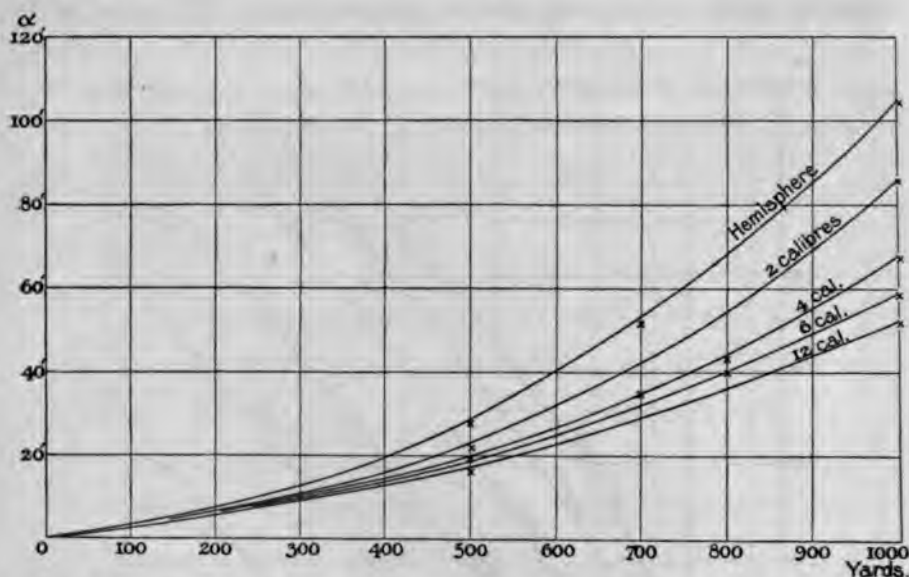


DIAGRAM IV.—Calculated and observed angles of elevation for ogival-headed projectiles of 0.5, 2, 4, 6, and 12 calibres radius.

Weight of projectile, 154 grains. Muzzle velocity, 2480 f.s.

Full curves are the calculated angles.

x are results of experiments.

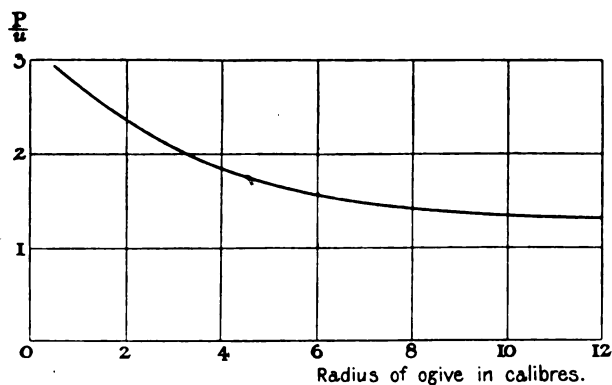


DIAGRAM V.— P/u in terms of radius of ogive.

P = average air resistance (in lb. per square foot) on the cross-section of the projectile.

u = velocity of projectile, 850 f.s.

* There is always a difficulty in ascertaining the true zero of the sighting of a rifle. It is well known that the first shot from a cold barrel gives a zero different from that indicated by the subsequent rounds, and that in firing a long series, the sighting for a

Whether the difference in the value of a requisite for these bullets is entirely due to the blunt points, must be decided by further experiment.

Sharp-pointed bullets are in use in several Continental countries at the present time, and I may notice that the trajectories computed by the formula, using the values of a obtained from Diagram III, agree very well with tables which have been arrived at by experiment in each case.

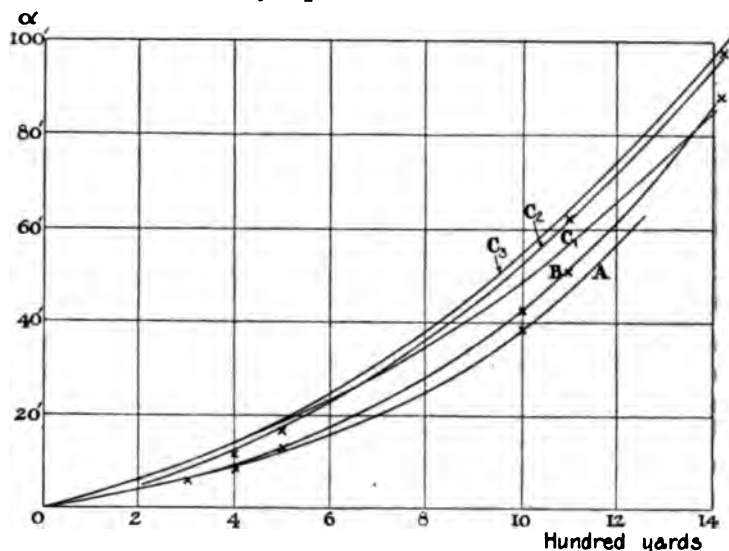


DIAGRAM VI.—Comparison of calculated and observed angles of elevation for ogival-headed projectile of 150, 154, and 225 grains. Radius of ogive 12 calibres.

Curve A refers to angles for sharp-pointed 150-grain projectile. Muzzle velocity 2360 ("a" deduced from the 154-grain projectile with muzzle velocity 2460 f.s.), "a" = 0.94.

Curve B refers to angles for same shape and weight but with flattened point ("a" in this case has to be increased to 1.12 to make the calculated and observed results agree).

Curve C₁ refers to angles for sharp-pointed 225-grain projectile with muzzle velocity of 2360 f.s. ("a" = 0.68.)

Curve C₂ refers to angles of the same shape but with flattened point as found by experiment.

Curve C₃.—Calculated angles for projectile of C₂. ("a" = 0.84.)

The crosses x are the results of experiment in each case.

It is a matter of some interest to see what advantage would be gained by giving these extreme pointed shapes to the projectiles of large guns. For this purpose I have prepared Diagrams VIII, IX, which give the angles of elevation and the ranges for a 6-inch and 12-inch gun, both having a muzzle given range has occasionally to be altered. It is probable, I think, that the differential cooling of the barrel may have to do with this, and may render the zero uncertain to the extent of a minute or two.

velocity of 2850 f.s. The upper curves refer to projectiles with ogival heads of two calibres, and the lower to 12-calibre heads. The gain with the 6-inch gun is considerable, but the ranges would have to be much over 10,000 yards to get a proportionate advantage with the larger gun.

Before leaving the subject of pointed projectiles, it may be remarked that the trajectories of projectiles differing either in shape, size, or weight, cannot be exactly similar, *i.e.*, differ from one another merely in scale, if only one of these quantities differ, for if they could, the angles of elevation would

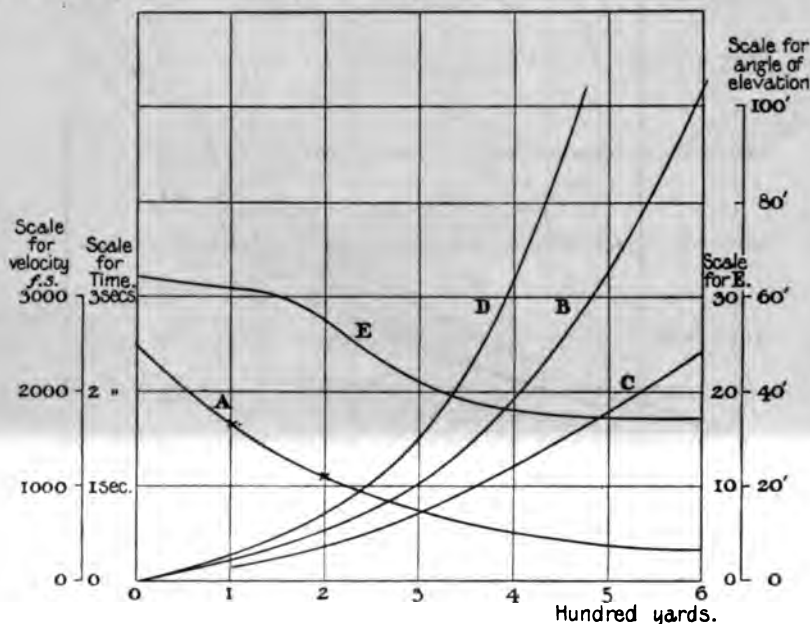


DIAGRAM VII.—Curves relating to a flat-headed projectile.

Weight, 154 grains.

Muzzle velocity, 2480 f.s.

A = calculated velocity.

X = velocity from ballistic pendulum experiments.

B = angle of elevation found by experiment.

C = calculated time of flight.

D = $g t^2 / 2R$.

E = value of g' (in f.s.s.) required to fulfil the condition $g' t^2 = 2Ra$.

be the same when one range was a certain definite multiple of the other. In this case the equation

$$g'_1 t_1^2 / 2s_1 = g'_2 t_2^2 / 2qs$$

must hold for all values of R (q_1 being the constant ratio of S_2/S_1). This leads to

$$q(1 - c(1 - e^{-a_1 t_1})) t_1^2 = (1 - c(1 - e^{-a_2 t_2})) t_2^2,$$

an equation which is obviously only satisfied for particular values of t .

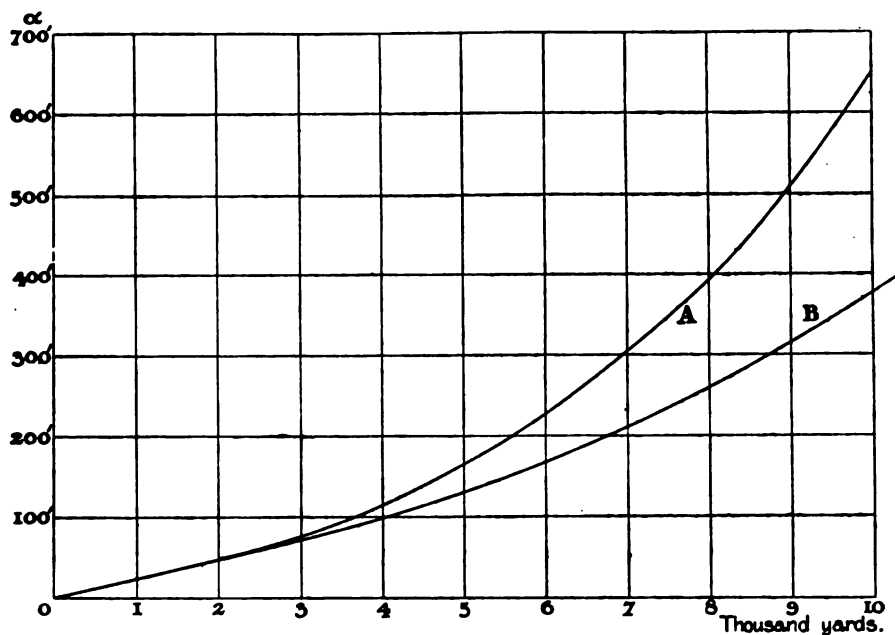


DIAGRAM VIII.—Angles of elevation for a 6-inch gun. Weight of projectile, 100 lbs.

Muzzle velocity, 2850 f.s.

A. Ogival head, 2 calibres radius.

B. " 12 " "

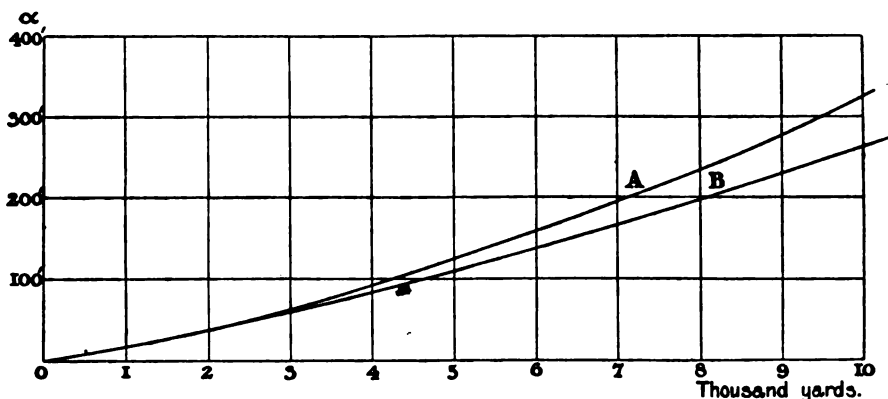


DIAGRAM IX.—Angles of elevation for a 12-inch gun. Weight of projectile, 850 lbs.

Muzzle velocity, 2850 f.s.

A. Ogival head, 2 calibres radius.

B. " 12 " "

The trajectories of two different projectiles will, however, be identical if $\frac{Pd^2}{uW}$ is the same for each. Within the limits for $\frac{P}{u}$ found in these experiments,* therefore, d may be varied in the ratio of $\sqrt{2}$ to 1 (W constant),

* See Diagram V.

and w in the ratio of 2 to 1 (d constant), the trajectory remaining the same, if a proper form of head is chosen.

It was mentioned at the beginning of this paper that the approximate formula used for pointed forms did not apply to the flat-headed projectiles. The reason for this is that the resistance they encounter is so large that their velocity falls to below 1000 f.s. (the lower limit of the formula) at comparatively short ranges. As regards accuracy, their shooting was bad at all distances, but excessively so at ranges exceeding 300 yards. Out of the large number of rounds fired, only one hit on the target at 700 yards was recognised. The initial velocity of the experimental flat-head was 2480 f.s. as it was with the other forms, but at 500 yards the air resistance had reduced this to under 400 f.s.

Although the simple range formula used for pointed forms will not on this account apply to the flat heads, their range in terms of time can readily be got from the resistance curve given in 'Roy. Soc. Proc.,' A, vol. 79, p. 273. Let f be the retardation experienced at velocity v , and η the negative velocity given to the shot by the retardation; then $v_0 - \eta =$ remaining velocity, $dt = d\eta/f$, and $t = \int f^{-1} d\eta$. Also $ds = \eta dt$, where s is the loss of range due to the negative velocity η ; hence the total space R , described in time t , is $v_0 t - \int \eta f^{-1} d\eta$. Now f is $\pi g d^2 / 4W \times$ resistance per unit area at velocity v ; and resistance per unit area is the ordinate in the resistance curve given in the paper above referred to. In order therefore to find the range in terms of time for any flat-headed projectile, we have only to find graphically, or otherwise, the integrals $\int f^{-1} d\eta$ and $\int \eta f^{-1} d\eta$, and to plot the second in terms of the first. The range is then $v_0 t - 4W / \pi g d^2 \times$ the ordinate; and the time of flight $4W / \pi g d^2 \times$ the abscissa.

For the purpose of comparing theory with the data obtained from firing, it is more convenient to plot in terms of range. This has been done in Diagram VII, where curves are given showing the remaining velocity, the time of flight, and the angle of elevation used in the experiments. The two crosses on the velocity curve are velocities obtained from ballistic pendulum experiments at 100 and 200 yards. A curve (E) is also added which gives the value which must be taken for g' in order that $g' t^2 / 2R$ may be equal to α . From the rapid drop in g' it is clear that as the range increases the axis of the shot must depart widely from the direction of motion; in fact, since the mean downward acceleration for the whole time of flight at 500 yards is only about 17 f.s.s. at that range, at least half the weight of the projectile must be borne on the air.

With larger projectiles the inaccuracy of shooting and loss of velocity would not be so conspicuous; for instance, a 12" flat-head, weighing 850 lbs., with

an initial velocity of 3000 f.s. would still have a velocity of 2200 f.s. at two seconds after its start and would have travelled 5150 feet, and it is not likely that any very great inaccuracy would declare itself up to ranges of 2000 or 3000 yards. Beyond this, however, the shooting would probably become more and more erratic.

One very remarkable feature about the behaviour of flat-headed projectiles is their great lateral drift. An ordinary pointed projectile has a small drift in the same direction as it would have if it rolled on the air under it. The flat-headed projectile drifts in the opposite direction, *i.e.*, as if rolled on the air above it. This difference has been noticed by Major-General Owen, 1862 and 1864, but the fact seems to have been held as doubtful. With the 10-gramme bullets, however, there could be no doubt about the matter, as the drift amounts to more than 80 inches at 500 yards.

I will not go further into the experiments made with this class of projectile at present, although their behaviour is likely to be of help at some future time in forming a true conception of the nature of the action of the air in controlling the attitude of the shot with regard to the trajectory.

Returning now to pointed projectiles, it will be seen from Diagram II that little is to be gained by using a form of head whose radius is greater than 12 diameters, and, in addition, if a more pointed form is used with a solid shot, comparatively little parallel body is left to give guidance in the barrel. The resistance might be further decreased if it were possible to use a pointed tail and so lessen the negative pressure on the base, but no mere rounding off of the base would do much in this direction, although it might well act to unstabilise the bullet. What is wanted is a tail so pointed that its angle is at any rate less than the angle of the cone over which the air naturally flows in passing into the wake of a flat-based projectile, and which is conspicuous in many of the photographs of flying bullets. These fish-formed bullets, however, are naturally unstable and almost as soon as started they set their axes at a definite and considerable angle to the direction of flight.

It would be possible, I believe, to keep them in a true course if they were provided with proper fins, and if we succeed in this, angles of elevation of 25' to 30' may be looked for as possible for small arms, at ranges of 1000 yards.

I have to give my best thanks to Colonel the Hon. T. F. Fremantle and Colonel H. Mellish for their co-operation and assistance in carrying out these experiments at their ranges at Wistow and at Hodsock Priory. All the rounds were fired by them, and their well-known skill as rifle shots made any sensible error in aiming a negligible quantity.

Note on the Ascent of Meteorological Balloons and the Temperature of the Upper Air.

By A. MALLOCK, F.R.S.

(Received March 11,—Read March 26, 1908.)

The recent investigation of the upper atmosphere by means of india-rubber balloons has led to the discovery that an almost constant temperature is reached when the pressure has decreased to about 150 mm. The lowest pressure reached in England is, I believe, a little under 50 mm., and the corresponding height about 20 kilometres.

I thought it might be of interest to examine, from a theoretical point of view, what the behaviour of balloons such as are used in meteorological work must be as regards the possible heights to which they might ascend and the variations of their velocity as they rise. The determining factors are:—

(1) The relative density of the gas in the balloon and of the outer air at the same pressure.

(2) The ratio of the dead weight of the balloon and fittings to the total lifting force at ground level.

(3) The compression, by the elasticity of the balloon, of the gas it contains.

As regards the velocity of ascent, the upward accelerating force is equal to the difference of the weight of the air displaced by the balloon and of the gas which fills it, less the weight of the balloon and its load. This is balanced by the resistance which, for the velocities dealt with, varies directly as the density of the air (ρ), as the square of the velocity (v), and as the square of the linear dimensions (r).

Let W be the weight of the balloon and fittings, F the total lifting force when the pressure outside is p_0 , and F_0 when it is $p = p_0/m$; also let e ($= p_0/n$) be that part of the pressure inside the balloon due to its elasticity, so that the actual pressure inside is $p + p_0/n$,* and $1/\kappa$ the ratio of the densities of the gas in the balloon and of the atmosphere at the same

* In this note it is assumed here that e does not vary with the height. This is not quite true: in reality, e decreases at first as the height increases, and finally becomes rather greater than it was at first. See 'Roy. Soc. Proc.,' vol. 46, p. 239, and vol. 49, p. 458.

pressure ($\kappa = 16$ for hydrogen). Then if u_0 is the volume of the balloon at pressure p_0 and density ρ_0 ,

$$F = gu_0\rho_0\left(\frac{p}{p+e}-\frac{1}{\kappa}\right); \quad F_0 = gu_0\rho_0\left(1-\frac{p_0+e}{\kappa p_0}\right); \quad (1)$$

therefore
$$\frac{F}{F_0} = \frac{n}{n+m} \frac{n(\kappa-1)+m}{n(\kappa-1)-1} = M, \text{ say.} \quad (2)$$

Also, if v_0 is the velocity with which the balloon would rise from the ground if it had no weight, and did not compress the gas by its elasticity (*i.e.*, if $n = \infty$ and $W = 0$), the ratio of the upward accelerations at pressures p and p_0 is $\frac{F-W}{F_0-W}$ or (if $W/F_0 = A$) $\frac{M-A}{1-A}$, which must be equal to the ratio of

the resistances experienced, viz., $\frac{\rho v^2}{\rho_0 v_0^2}$. Now

$$\rho/\rho_0 = 1/m, \quad \text{and} \quad \frac{v^2}{v_0^2} = \frac{1}{m^{\frac{1}{2}}} \left(\frac{n+1}{m+n} \right)^{\frac{1}{2}};$$

hence
$$\frac{v}{v_0} = m^{\frac{1}{2}} \cdot \left(\frac{m+n}{m+1} \right)^{\frac{1}{2}} \cdot \left(\frac{M-A}{1-A} \right)^{\frac{1}{2}}. \quad (3)^*$$

Thus the velocity of the balloon at first increases as the one-sixth power of the ratio of the density of the air at the elevation attained to the density at ground level,[†] and when n is large (that is when the elastic compression is small) the upward velocity reaches its maximum not far from the greatest elevation to which the balloon can attain.

The balloon will cease to ascend when $F = w$, and this leads to the following expression for the limiting value of m :—

$$m = \frac{n^2(\kappa-1)(1-A)+nA}{A(n(\kappa-1)-1)+n}. \quad (4)$$

The pressure is then $760/m$ mm.

The results of equations (3) and (4) are traced in diagram I, the values for s and n being such as are likely to be met with in practice. It is remarkable how rapidly the velocity decreases as the minimum pressure is approached.

To connect the pressure with the height at which it is experienced, the temperature at every point of the ascent must be known, and this information is furnished by the automatic recorder attached to the balloon.

I thought it might be of interest to compare the actual temperatures with

* Equation (3) assumes that the temperature remains constant. The effect of the temperature falling with the pressure is to reduce the ratio v/v_0 .

† The reason being that the decrease in density rather more than compensates for the effect of the increased cross-section.

the adiabatic temperatures, *i.e.*, the temperature which a given volume of dry air would have if transported from ground level to a given height and allowed to expand without receiving or losing heat.

The height at which the pressure p is found in these circumstances is (if H = height of homogeneous atmosphere) $h = H \frac{\gamma}{\gamma-1} (1 - m^{-\frac{\gamma-1}{\gamma}})$, which gives a finite limit to the height of the atmosphere at 27 kilometres nearly. The ratio of the absolute temperatures at p and p_0 is $\theta/\theta_0 (1/m)^{\frac{\gamma-1}{\gamma}}$.

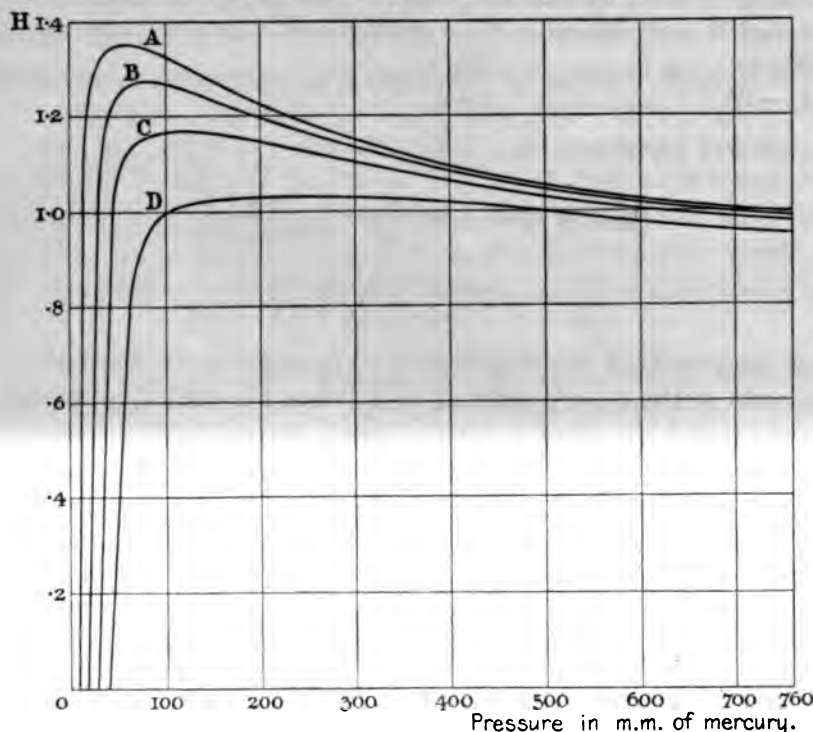


DIAGRAM I.—Velocity of Ascent of Balloons.

The ordinates give the ratio of the velocity of a balloon in air at pressure p , carrying a load $0.6 F_0$, and with internal pressure $= p + \frac{p_0}{n}$, to the velocity at p_0 of the same balloon if devoid of weight, and with the external and internal pressures equal. For A, $n = 100$, for B = 75, C = 50, D = 30.

For isothermal expansion $dh = dHp_0/p$, and if the arbitrary relation between temperature and pressure found from the balloon records is $\theta/\theta_0 = \phi(p)$, the actual value of dh is $dH\phi(p) p_0/p$, the integral of which can readily be found graphically.

The relations of the height corresponding to a given pressure on the

supposition of: (1) constant temperature; (2) temperature as observed; (3) adiabatic temperature, are given in diagram II, and it is worthy of notice that the observed decrement of temperature is almost exactly 0.7 time the

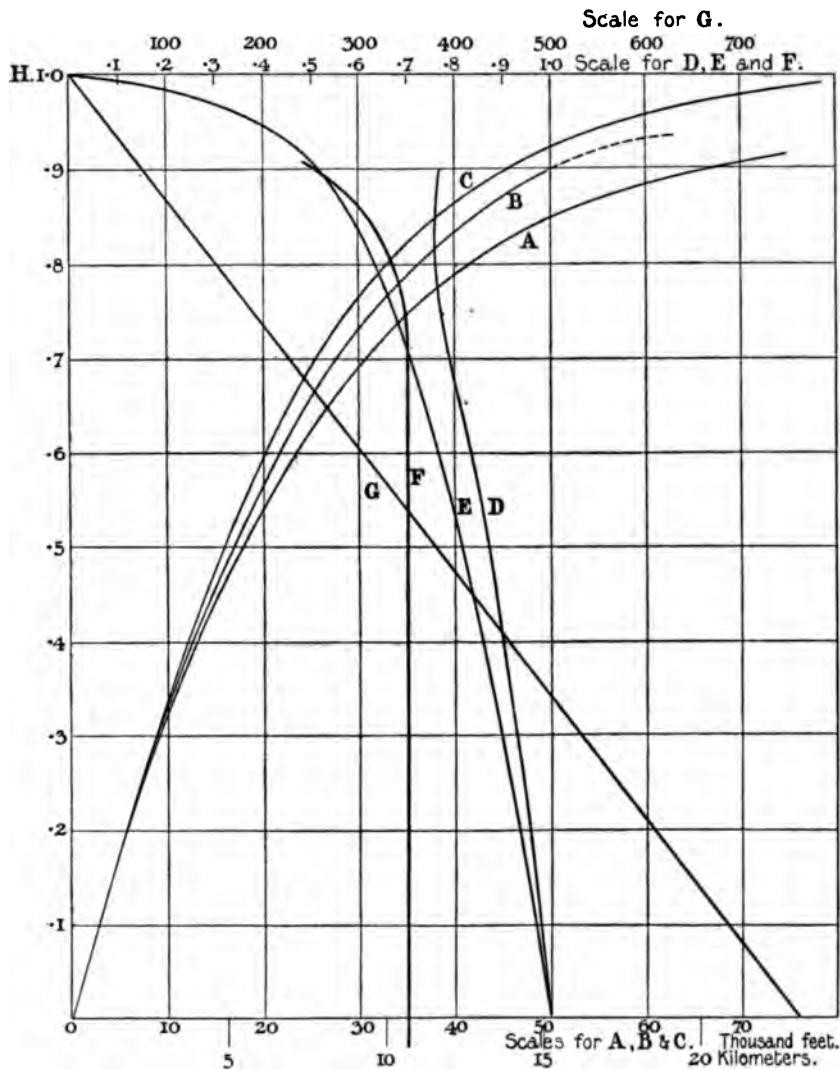


DIAGRAM II.

The ordinates are fractions of the height of the homogeneous atmosphere. The abscissæ of Curves A, B, C, are heights at which pressure given by ordinates is found; A at constant temperature, B as observed, C with adiabatic expansion. The abscissæ of Curves D and E are the ratio of the absolute temperatures; D as observed, E with adiabatic expansion. Curve F is ratio of observed decrement of temperature to adiabatic decrement. Curve G gives, in millimetres of mercury, the pressure equivalent to the heights in A, B, C.

adiabatic decrement down to a pressure of rather less than 200 mm., corresponding to a height of 11 kilometres. (See curves D, E, and F on the same diagram.)

The balloon observations have brought out the fact that at this pressure or thereabouts the temperature ceases to change with the height and remains between -50° and -60° C. up to the greatest height (approaching 20 kilometres) to which the balloons have ascended.

Greater heights than this could probably be reached if the balloons were made more expansible, *i.e.*, if the unfilled balloons were of thinner material and larger in volume than those at present in use, as this would allow of the same lifting force for the given quantity of gas, and give more scope for expansion with diminished pressure.

I have to thank the Meteorological Office and Mr. W. H. Dines, F.R.S., for their kindness in giving me the requisite information concerning the observed temperatures and pressures obtained from the balloon records, and for details of the dimensions and weights of the balloons and apparatus.

On the Use of Iridium Crucibles in Chemical Operations.

By Sir WILLIAM CROOKES, D.Sc., F.R.S.

(Received and read May 7, 1908.)

I should like to draw the attention of chemists to the great advantages of using crucibles of pure iridium instead of platinum in laboratory work.

Through the kindness of Messrs. Johnson and Matthey I have had an opportunity of experimenting with crucibles of wrought iridium, and have used one for several months in the usual operations of quantitative analysis in my laboratory.

Iridium is as hard as steel, and the crucible is almost unaffected by any mechanical treatment that can reasonably be applied to it.

Brightly polished iridium superficially oxidises with a bluish colour when heated to redness, but it is reduced again on raising the heat. Repeated experiments, however, have shown that no appreciable alteration of weight is thereby caused.

Heated for some hours over a Bunsen burner insufficiently supplied with air the iridium crucible is unaffected and the deposit of carbon easily burns away, leaving the surface of the metal uninjured. All chemists know how seriously a platinum crucible is attacked in these circumstances. Iridium does not blister after long use, and it is unaffected by sulphur in the gas.

The crucible has been boiled in a beaker with aqua regia for several hours, the liquid evaporated down, fresh acids added, and the whole boiled down again. There was no appreciable loss of weight.

Microcosmic salt was fused in the crucible at a good heat for four hours, with frequent additions of carbon; a mixture of magnesium pyrophosphate and carbon has been ignited in it for four hours; and phosphoric acid and carbon have been heated together for some hours in it. In none of these cases was there any loss of weight or apparent action on the metal.

Silica and silicates, with a reducing agent, may be strongly heated in it for some time without forming a silicide or affecting the crucible.

Caustic potash fused at a red heat in the crucible attacks it, but not so strongly as it would have attacked platinum in the same conditions.

The crucible was heated to whiteness and melted lead was poured in. The lead then was boiled away at a white heat. There was no action on the crucible, and after cleaning with acids it appeared unchanged, with no alteration of weight.

Zinc was melted in it at a red heat and partially boiled away. On cleaning

with acids the crucible was unaffected. Zinc and acid zinc chloride (soldering fluid) were then heated in the crucible so that the zinc could "wet" it. The heat was then raised to the volatilising point of zinc for some time. On cleaning with acid the surface of the metal was seen to be superficially attacked, and the crucible had lost a few milligrammes in weight.

Copper melted in the crucible for some time makes it "hot rotten," *i.e.*, it is brittle while hot. But if the copper is well burnt off at a high heat the iridium reverts to its original condition.

Nickel, gold and iron can be melted and kept liquid in the crucible for some time, and then poured off with no injury to the crucible.

I have asked Messrs. Johnson and Matthey to make experimental crucibles of rhodium, ruthenium and osmium. The latter two metals they have not yet succeeded in fashioning, but I have been enabled to try similar experiments to those described above with a rhodium crucible, and I find it practically as resistant in all cases as iridium.

The low density of rhodium (11 as against iridium 22) would be a great advantage in quantitative operations, as the weight of a rhodium crucible would be only half that of one made of iridium, and the cost would be somewhat less.

*On the Measurement of the Atmospheric Electric Potential
Gradient and the Earth-air Current.*

By C. T. R. WILSON, F.R.S.

(Received March 4,—Read March 19, 1908.)

In previous papers* I have described a method of measuring the charge upon and current through a conductor exposed to the earth's electrical field and maintained at zero potential. The present paper contains an account of a series of such measurements, taken primarily with the object of testing the method, and, in particular, of gaining some evidence as to whether it is legitimate to deduce from the "dissipation factor," found for the exposed "test-plate" of the apparatus, the current from the atmosphere into each square centimetre of the ground when the potential gradient is known.

With the object of gaining information on this question, alternate measurements were made with the apparatus in its ordinary condition, and with its test-plate covered with turf. It was thought that if the ratio of the current to the charge on the exposed surface were found to be the same in the two cases, it might with some confidence be assumed that the same ratio would hold for the current and charge per unit area of the ground. As will be seen later, the ratio of the current to the charge remained within the limits of experimental error unaltered when the test-plate was covered with turf.

The charge on an exposed earth-connected conductor, always maintained in the same position relative to the ground and other objects, may be taken as proportional to the charge per square centimetre of the neighbouring level ground, or to the potential gradient. Experiments were therefore made to determine the factor by which the charge on the test-plate had to be multiplied to give the charge per square centimetre of the ground. This having been done, the measurements made with the test-plate require merely to be multiplied by the appropriate factor to give the charge per square centimetre of the ground, and also the current entering each square centimetre of the ground.

The observations were carried out on the farm of Hundleshope, about three miles from Peebles and about 25 miles south of Edinburgh.† From September, 1906, till April, 1907, inclusive, the place of observation was on a nearly

* 'Cambridge Phil. Proc.,' vol. 13, pp. 184 and 364, 1905—6.

† I take this opportunity of acknowledging my indebtedness to Mr. Brownlee, of Hundleshope, for his kindness in affording me every facility in carrying out these observations.

level field in the bottom of a valley, about one mile wide, lying between hills rising on the north to 1314 feet (Cade-muir), and on the south to 2248 feet (Hundleshope Heights), the bottom of the valley being about 700 feet above sea level. The later measurements were taken a few hundred yards to the south of this point, just within the mouth of a smaller tributary valley, also flat-bottomed, in which the grass was kept short by sheep.

Apparatus and Method.

The apparatus only differed in dimensions and in minor details from that described in the previous papers already referred to.* The electrometer used is a gold leaf instrument of a type suitable for the measurement of potentials only differing slightly from zero; the essential feature of the instrument being that the gold leaf hangs within an inner case, maintained at a suitable constant potential by means of a quartz Leyden jar.

Supported by an upward prolongation of the vertical metal rod which carries the gold leaf is a horizontal blackened brass disc, the "test-plate," 7 cm. in diameter; it is provided with an earth-connected guard ring (external diameter = 17 cm.), from which it is separated by an annular air gap $2\frac{1}{2}$ mm. wide. A cylindrical cover rests upon the guard ring, and shields the test-plate, except when it is to be exposed to the influence of the earth's electrical field.

If the conducting system which includes the gold leaf and test-plate is momentarily earthed, and the cover is then removed (the apparatus being freely exposed in the open air), the gold leaf will be displaced, its potential being raised if the electrical field is in the normal direction of fine weather. The potential is at once brought back to zero by means of a "compensator"; the reading of the compensator when the reduction to zero potential is effected serves to measure the charge now held on the upper surface of the test-plate. The charge measured is what would exist on the upper surface of the test-plate if it were earth-connected.

If the exposure be continued for a short time, the compensator being adjusted as may be necessary to keep the test-plate at zero potential, and the cover be then replaced, the charge which has entered the test-plate from the atmosphere in a known time may be determined, *i.e.*, the current from the atmosphere into the test-plate when exposed under the same conditions as an earth-connected body.

The compensator actually used had the form of a cylindrical condenser, of which the inner conductor was a metal rod connected to the gold leaf system,

* The apparatus was made by the Cambridge Scientific Instrument Company.

the outer conductor being a brass tube, maintained during any series of observations at a constant negative potential by means of a quartz Leyden jar, and capable of sliding parallel to its length to give a variable capacity.

The capacity of the conducting system, which included the gold leaf and its supporting rod, the compensator rod and the test-plate, was measured according to the method described in the previous paper.* Under standard conditions, *i.e.*, with the cover over the test-plate and the compensator tube drawn out to its zero position, it amounted to 15.2 cm.

The calibration of the compensator was also carried out by the method described in the same paper. It was found to be an improvement to have the central rod of the compensator somewhat longer than in the instrument there described; by this means the calibration curve was made to approximate very closely to a straight line throughout its length, *i.e.*, the displacement of the compensator tube required to bring the potential of the gold leaf system to zero is very nearly proportional to the charge to be measured.

The displacement of the gold leaf per volt amounted to 2 divisions of the eye-piece micrometer of the reading microscope over the range of deflections used.

The electrometer, with its test-plate and guard ring, rested, during the open-air observations, on the top of the wooden box in which the instrument was kept when not in use, the height of the test-plate and guard ring above the ground being then 70 cm. The observer reclined on the ground, and, having his eye at the microscope and his hand on the compensator, always occupied the same position relative to the apparatus.

In making a series of observations, the following was the usual order of operations. The cover was placed on the guard plate, the compensator was pushed through a definite number of scale-divisions from its zero or standard position, the gold leaf system was then momentarily earthed and the compensator drawn back to its zero position; the gold leaf deflection was then read. The charge corresponding to this deflection is known from the sensitiveness of the electrometer (the deviation per volt), and the capacity of the gold leaf system under standard conditions, and it requires for its neutralisation a known displacement of the compensator—from zero to the position which it occupied when the gold leaf system was earthed. The charge corresponding to any other displacement of the compensator is then known from the calibration curve. This test only required to be performed two or three times in the course of a day's observations on account of the high insulation of the quartz Leyden jar which maintained the potential of the sliding tube of the compensator.

* 'Cambridge Phil. Proc.,' vol. 13, p. 363, 1906.

The gold leaf system was again momentarily earthed (the compensator being in its zero position), and at a definite instant, as indicated by a watch hung from the support of the microscope, the cover was removed. The compensator was at once pushed in to bring the gold leaf (deflected on removing the cover) back to its zero position. The compensator reading was noted; this gives the charge on the upper surface of the exposed test-plate when earth-connected. The exposure was continued for a definite number of minutes (generally from two to five), the compensator being moved as might be required to keep the gold leaf system at zero potential.

When the desired time of exposure was completed, the cover was replaced and the compensator drawn out to its zero position. The gold leaf reading was now taken, the gold leaf system being then earthed and the new zero reading taken. The difference between the last two readings, the sensitiveness of the electrometer and the capacity of the gold leaf system being known, gives the charge which has entered the test-plate from the atmosphere during the exposure.

Finally the cover was again removed and a second reading of the charge on the test-plate obtained as before.

An exactly similar set of readings was made with a circular piece of turf, held in a shallow tinplate box above which it projected for two or three centimetres, resting on the test-plate. The capacity of the gold leaf system, with the turf on the test-plate and the cover over it, was determined by comparing the deflection of the gold leaf, initially at its zero position, which was produced by drawing out the compensator to its standard position from a given initial position, with that produced by the same operation in the absence of the turf. The potential differences, corresponding to the same charge for the gold leaf system with and without the turf on the test-plate, were thus compared. This determination of the capacity having been made, the other operations which have been described for the test-plate enabled the charge upon and current through the turf to be measured. The same piece of turf was generally used throughout a day's observations. The charge on the turf was generally about three times that on the test-plate alone.

RESULTS.

(1) *Comparison of the Dissipation from Different Exposed Surfaces.*

The dissipation factor is expressed as the percentage of the charge on an earth-connected exposed body which is neutralised per minute. I give first the results of some comparisons which were made of the dissipation from the test-plate and from a cylindrical metal cylinder resting on the test-

plate. The cylinder was a tinplate box 5 cm. in diameter and 2.6 cm. high. The charge on the box when exposed to the earth's field and at zero potential was found to be about 2.3 times that on the test-plate under the same conditions.

Under dissipation are given the means of the dissipation factors for each day.

Table I.

| Date. | Dissipation. | | Number of comparisons. | Charge on test-plate. | Remarks. |
|----------------|--------------|-----------|------------------------|---------------------------|-----------------------|
| | Plate. | Cylinder. | | | |
| 1907. | per cent. | per cent. | | | |
| Sept. 9 | 5.1 | 4.7 | 3 | 8.6×10^{-2} E.U. | Calm, sunshine. |
| Sept. 10 | 4.7 | 4.7 | 4 | 18.4 " | Calm, hazy, sunshine. |
| Sept. 13 | 10.8 | 12.3 | 4 | 6.0 " | Clear, overcast. |
| Sept. 28 | 9.5 | 9.2 | 6 | 9.7 " | Clear, sunshine. |
| Oct. 1 | 4.5 | 4.2 | 4 | 11.4 " | Overcast. |
| Mean | 6.9 | 7.0 | — | — | |

There is no indication of any marked difference in the dissipation factors.

In the following table are given the results of a series of comparative measurements of the dissipation, made alternately with the ordinary test-plate of the instrument and with a piece of turf, placed in a shallow tinplate tray, resting on the test-plate; the test-plate was completely covered by the turf. The dissipation factor is calculated by finding the ratio of the charge gained by the exposed conductor per minute to the mean of the charges on the conductor at the beginning and end of the exposure, the potential of the system being maintained at zero throughout. The dissipation factors given for each day are the means of all the observations of this comparison series taken on that day; the number of the comparisons made is given, as well as the mean charge on the exposed test-plate during these observations.

This series gives practically the same mean value for the dissipation from both test-plate and turf, and there is, on the whole, pretty good agreement for the individual days. There is, however, a rather serious discrepancy on August 30, when the mean dissipation from the turf is considerably in excess of that from the test-plate. Both the intensity of the electric field and the dissipation were, however, very variable on that day, and the difference is probably accidental. There is no evidence of any tendency for

a difference to show itself on calm days with bright sunshine, when any specific photo-electric effect in the case of either the turf or the test-plate might have been expected to make itself manifest. Days of bright sunshine were not, as a matter of fact, days of unusually high dissipation.

Table II.

| Date. | Dissipation. | | Number of comparisons. | Charge on plate. | Remarks. |
|---------------|--------------|-----------|------------------------|---------------------------|--|
| | Plate. | Turf. | | | |
| 1906. | per cent. | per cent. | | | |
| Sept. 29..... | 9.7 | 9.1 | 11 | 6.8×10^{-2} E.U. | Clear sky, bright sun, calm. |
| Oct. 1..... | 8.1 | 8.3 | 4 | 10.9 " | Sky nearly covered; wind, from S.W. at first, died away. |
| 1907. | | | | | |
| Jan. 8..... | 7.5 | 7.6 | 4 | 7.5 " | Overcast, wind from W. fairly strong. |
| Jan. 10..... | 13.9 | 15.3 | 6 | 6.1 " | Sun hidden, clear, bright; wind from W. |
| Jan. 14..... | 12.1 | 13.2 | 3 | 5.4 " | Overcast, hill tops in cloud, clear below. |
| Apr. 6..... | 17.4 | 18.7 | 7 | 6.6 " | Very clear, wind from W. |
| Apr. 18..... | 3.0 | 3.1 | 4 | 7.5 " | Calm, nearly cloudless, sunshine. |
| July 3..... | 7.2 | 7.5 | 6 | 6.7 " | Overcast, clear atmosphere. |
| July 5..... | 6.0 | 4.4 | 3 | 7.1 " | Sky nearly covered with cumulus. |
| Aug. 30..... | 11.4 | 14.2 | 6 | 6.5 " | Clear, cumulus about. |
| Sept. 7..... | 8.8 | 7.9 | 6 | 9.8 " | Clear, cumulus about, variable wind. |
| Sept. 9..... | 5.3 | 4.1 | 7 | 7.7 " | Calm, almost cloudless, haze. |
| Sept. 10..... | 6.46 | 6.24 | 11 | 17.9 " | Cloudless, calm, hazy, hot sun. |
| Sept. 13..... | 10.8 | 12.4 | 4 | 19.3 " | Clear atmosphere, overcast. |
| Sept. 28..... | 9.5 | 8.9 | 4 | 9.8 " | Bright sun, almost cloudless. |
| Oct. 1..... | 4.5 | 3.5 | 4 | 11.4 " | Overcast, clouds touching hills, haze below, wind fairly strong. |
| Means | 8.85 | 9.02 | — | 9.2×10^{-2} E.U. | |

The charge on the turf was always about three times as large as that on the exposed test-plate; it is, moreover, concentrated on the tips of the projecting grass blades; the conditions are, therefore, very different in the two cases. The agreement is sufficiently good to afford strong grounds for assuming a definite dissipation factor depending on the condition of the atmosphere. Further comparisons for very weak fields are, however, desirable.

It is, perhaps, of interest to add the results of the individual comparisons for one day. I give those of September 10, 1907, a calm day with ~~cloudless~~ sky but some haze, most of which was dissipated in the early ~~afternoon~~. The electrical field was unusually steady.

Table III.—September 10, 1907. Quantities given in Hundredths of an Electrostatic Unit.

| Time. | Charge. | | Leak per minute. | | Dissipation. | |
|----------------------|-------------|-------|------------------|-------|--------------|-----------|
| | Test-plate. | Turf. | Test-plate. | Turf. | Test-plate. | Turf. |
| | | | | | per cent. | per cent. |
| 10.41—10.46 A.M. ... | 17.2 | — | 0.35 | — | 2.0 | — |
| 11. 6—11.19 ... | 17.6 | 39.2 | 0.71 | 1.73 | 4.0 | 4.4 |
| 11.23—11.35 ... | 19.2 | 58.0 | 0.81 | 2.42 | 4.2 | 4.2 |
| 11.40—11.52 ... | 17.6 | 51.4 | 0.91 | 3.95 | 5.2 | 5.9 |
| 11.58—12.10 P.M. ... | 19.6 | 58.0 | 1.72 | 4.25 | 8.8 | 7.3 |
| 12.39—12.45 ... | 18.8 | 53.0 | 1.52 | 4.8 | 8.1 | 9.2 |
| 1.10—1.16 ... | 15.7 | 47.0 | 1.52 | 3.8 | 9.8 | 8.1 |
| 1.19—1.26 ... | 18.4 | 58.0 | 1.65 | 4.0 | 9.0 | 6.9 |
| 1.30—1.38 ... | 16.1 | 51.5 | 1.27 | 4.15 | 7.9 | 8.1 |
| 1.40—1.47 ... | 14.9 | 44.5 | 0.76 | 2.28 | 5.1 | 5.1 |
| 1.53—2. 0 ... | 17.2 | — | 0.89 | — | 5.2 | — |
| 2. 6—2.18 ... | 19.6 | — | 0.91 | — | 4.6 | — |
| 2.30—2.44 ... | 19.6 | 56.0 | 0.91 | 2.76 | 4.6 | 4.9 |
| 3. 9—3.23 ... | 19.4 | 53.5 | 0.86 | 2.42 | 4.4 | 4.5 |
| 3.39—3.44 ... | 25.8 | — | 1.24 | — | 5.0 | — |

(2) *Charge and Vertical Current per Unit Area of the Ground.*

The results contained in the foregoing tables afford fairly strong grounds for assuming, for a given place of observation, that the fraction of the charge per unit area of the ground which is neutralised per minute is the same as that found for the test-plate of the apparatus. It seemed desirable, therefore, to determine the factor by which the charge on the exposed earth-connected test-plate has to be multiplied to give the charge per square centimetre of the ground in the immediate neighbourhood, sufficiently far away, however, to be unaffected by the presence of the observer and apparatus. The same factor, if the dissipation factor be assumed to be the same for the ground as for the test-plate of the instrument, will serve to deduce the current per square centimetre of the ground from that through the test-plate, which is directly observed.

For the purpose of determining this reduction factor, a large test-plate, which could be placed with its upper surface very little raised above the surface of the ground, was made; it was provided with a guard plate. The test-plate and guard plate were of wood, which was found to conduct sufficiently well for the purpose; the test-plate was 12 inches square, the guard plate was also square, the sides being 24 inches in length. The gap between them was $\frac{1}{4}$ inch wide. The guard plate and test-plate formed the roof of a shallow box, the total height from the upper surface of the roof to the under surface of the base being 2 inches, and the space between them

being 1 inch. The test-plate rested on three feet embedded in sulphur plugs filling cylindrical holes bored half-way through from its under side. A wooden cover, 17 inches square inside, rested on the guard plate, there being a space of 2 inches between the test-plate and the roof of the cover. A V-shaped notch was cut in one side of the cover to allow the passage of a wire between the test-plate and the electrometer. The wire was attached to the lower surface of the wooden test-plate, efficient contact being ensured by means of a sheet of tinfoil gummed over the wire and the surrounding wood. The wire led from the large wooden test-plate to a terminal which could be fixed on the upper surface of the ordinary test-plate of the instrument. In the actual experiments the horizontal distance between the centres of the two test-plates was about 90 inches, the vertical height of the small test-plate being in these, as in all the measurements, about 28 inches above the ground. Alternate measurements were made of: (1) the charge on the small test-plate, on removing its cover and bringing to zero potential by means of the compensator, and (2) of that on the large test-plate, the same method of removing its cover and bringing the potential of the system to zero by the compensator being used. In making the measurement of charge on the large plate, the terminal attached to the connecting wire was placed on the small test-plate (the other end of the wire being permanently attached to the large test-plate), the gold leaf system, with test-plates and connecting wire, was momentarily earthed, and the large cover removed to a distance, the compensator being then adjusted to bring the gold leaf to its zero reading and the cover at once replaced. The compensator reading required to give zero potential was then read again; if the operations were sufficiently quickly gone through and the electrical field was not too variable, the last reading was generally zero, the time of exposure being short enough to prevent any appreciable gain of charge from the atmosphere. Since the small test-plate and the connecting wire were exposed even when the large test-plate was covered, any change of field during the time required for an observation to be completed was troublesome. It was found convenient to have an assistant to remove the cover and to replace it according to signal, as the time required for an observation was thereby shortened. On removing the cover the assistant retired to a distance of several yards, at which distance it was found by trial that he was without effect on the field at the large test-plate. The presence of the electrometer and observer were also without any marked effect on the charge on the large test-plate. To test this point it would be sufficient to place conductors of similar size and shape at an equal distance on the other side of the large test-plate and observe whether any effect was produced on removing them to a distance or replacing them. An approximation to a test of this kind was

effected by stationing the assistant at the point referred to and looking for any displacement of the gold leaf as a consequence of his rising from a lying to a sitting posture. No such displacement could be observed.

It was necessary to make a large number of comparisons of the charges on the large and small test-plates when exposed to the electric field of the earth and brought to zero potential, on account of variations in the potential gradient. The mean of 12 such comparisons, made on March 29, gave 5.65 for the ratio of the charge on the large plate to that on the small test-plate. The observations on this day were carried out without assistance, and the time taken to complete an observation with the large plate was generally long enough to cause a measurable charge to be gained by the plate, which was detected on replacing the cover. On April 1, a longer series of observations was made with the help of an assistant, and in 13 of the comparisons of charge no appreciable charge was gained by the large test-plate. The mean of the ratios of the charges on the test-plates given by these 13 comparisons was 5.60. The mean of 10 other comparisons of the same ratio, in which a correction had to be made for the charge gained by the large test-plate, amounted to 5.66. The value of the ratio obtained from the observations to which no correction had to be applied (5.60) is the one used in the calculation of the reduction factor.

The effective area of the small test-plate (obtained by adding half the area of the gap to that of the test-plate) is 41.3 sq. cm., that of the large test-plate, obtained in the same way, 968 sq. cm., the ratio of the areas being 23.4. This gives for the ratio of the surface density of the electrification on the small test-plate to that on the large, 4.2. The density on the large test-plate, 12 inches square, at a height of 2 inches above the surface of the ground, and surrounded by a guard plate making up the flat surface exposed to an area four times that of the test-plate, has been taken as not differing appreciably from that on the general surface of the ground. The ground was not sufficiently flat, nor the grass sufficiently short, to make it appear worth while to attempt to determine the correction to be applied. The mean density of the electrification upon the exposed test-plate when at zero potential has been taken as being 4.2 times that upon the surface of the ground.

In the table which follows are given the charge and current per square centimetre of the ground in electrostatic units, deduced from the corresponding quantities for the test-plate, by multiplying by the appropriate factor. The charge and current per square centimetre of the ground are also given in coulombs and amperes, the potential gradient deduced from the charge being also given in volts per metre. In each case the values given are the means for the day over the range of time named in the first column.

Table IV.

| Date. | Time. | Charge per square centimetre. | | Current per square centimetre. | | Dissipation (per cent. per minute). | Potential gradient (volts per metre). |
|-------------|-------------------|-------------------------------|------------------------|--------------------------------|------------------------|---|---|
| | | E. U.'s. | Coulombs. | E. U.'s. per minute. | Amperes. | | |
| 1906. | September 29..... | | | | | | |
| | October 1..... | | | | | | |
| | October 8..... | | | | | | |
| 1907. | September 29..... | 11.45 A.M.—1.37 P.M. | 39.0×10^{-5} | 3.8×10^{-3} | 2.1×10^{-16} | 9.7 | 148 |
| | October 1..... | 3. 9 P.M.—4.15 P.M. | 61.5 " | 5.1 " | 2.8 " | 8.2 | 231 |
| | October 8..... | 3. 3 P.M.—4.18 P.M. | 68.3 " | 5.1 " | 2.8 " | 7.4 | 256 |
| | January 8..... | 3.43 P.M.—4.19 P.M. | 43.5 " | 3.6 " | 2.0 " | 8.2 | 164 |
| | January 10..... | 11.52 A.M.—12.44 P.M. | 35.4 " | 4.9 " | 2.7 " | 13.8 | 132 |
| | January 14..... | 11.47 A.M.—12.24 P.M. | 32.0 " | 3.8 " | 2.1 " | 11.6 | 120 |
| | April 6..... | 11.35 A.M.—12.38 P.M. | 38.4 " | 6.15 " | 3.4 " | 16.1 | 144 |
| | April 18..... | 11.25 A.M.—12.18 P.M. | 43.5 " | 1.28 " | 0.71 " | 2.9 | 163 |
| | July 3..... | 11. 5 A.M.—12. 3 P.M. | 38.9 " | 2.8 " | 1.6 " | 7.2 | 146 |
| | July 5..... | 11.13 A.M.—11.56 A.M. | 41.2 " | 2.4 " | 1.3 " | 6.0 | 154 |
| | August 30..... | 11.29 A.M.—12.42 P.M. | 37.8 " | 4.2 " | 2.3 " | 11.4 | 142 |
| | September 7..... | 11.25 A.M.—12.40 P.M. | 56.9 " | 5.05 " | 2.8 " | 8.8 | 214 |
| | September 9..... | 10.36 A.M.—2.40 P.M. | 50.0 " | 2.7 " | 1.5 " | 5.3 | 189 |
| | September 10..... | 10.41 A.M.—3.44 P.M. | 107.0 " | 6.2 " | 3.4 " | 5.9 | 401 |
| | September 13..... | 11.16 A.M.—12.23 P.M. | 29.6 " | 3.1 " | 1.7 " | 8.6 | 111 |
| | September 28..... | 10.56 A.M.—12.28 P.M. | 56.1 " | 5.5 " | 3.1 " | 9.8 | 211 |
| | October 1..... | 11. 9 A.M.—12.30 P.M. | 66.1 " | 2.8 " | 1.6 " | 4.5 | 249 |
| Means | | 49.7×10^{-5} | 16.6×10^{-14} | 4.03×10^{-3} | 2.22×10^{-16} | 8.55 | 187 |

The results given in the above table may be divided into three groups according to the type of weather on the different days. The following days were calm, with practically cloudless sky and bright sunshine, with a certain amount of haze: September 29, 1906, April 18, September 9, 10, and 28, 1907. The atmosphere was very clear, with a considerable amount of cumulus about, on January 10, April 6, July 5, August 30, and September 7, 1907. The sky was almost completely overcast on October 1, 1906, January 8 and 14, July 3, September 13, and October 1, 1907. The dissipation factor was least (mean = 6.6 per cent. per minute) for the cloudless, calm days, greatest (mean = 11.2 per cent. per minute) for the days with cumulus and clear atmosphere, the overcast days giving an intermediate value (mean = 8.05 per cent. per minute).

It is remarkable how nearly the mean value found for the current per square centimetre of the ground (2.2×10^{-16} ampere) agrees with that deduced by Gerdien* (2.4×10^{-16} ampere) from the results of measurements of conductivity and potential gradient. The agreement is no doubt to some extent accidental; a systematic series of regular observations extending over a considerable period would be required before a trustworthy mean value of the current could be obtained.

* Gerdien, 'Physikal. Zeitschr.,' Jahr. 6, 1905.

*On the Hysteresis Loss and other Properties of Iron Alloys
under very Small Magnetic Forces.*

By Professor ERNEST WILSON, V. H. WINSON, and G. F. O'DELL.

(Communicated by Sir William H. Preece, K.C.B., F.R.S. Received March 18,—
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The materials chosen for these experiments are the invention of Mr. R. A. Hadfield, and were supplied by Messrs. Sankey and Sons. They are an alloy of iron called "Stalloy,"* and a sample of transformer iron called "Lohys." The principal object of the research is to find the magnetic qualities of these materials when subjected to very small magnetic forces.

The specimens for the magnetic tests are in the form of rings composed of stampings wound with a primary and secondary coil, the secondary next to the core. The Stalloy stampings are separated by a thin coating of "insuline," and the Lohys stampings have paper insulation between every ten stampings. The particulars of the rings are given in Table I. The

Table I.

| Material. | Diameter of ring, cm. | | Mean thickness of stampings, cm. | Net sectional area, sq. cm. | Length of mean line, cm. | Primary turns. | Secondary turns. |
|--------------|--------------------------|-----------|--|--------------------------------------|-----------------------------------|-------------------|---------------------|
| | Internal. | External. | | | | | |
| Stalloy..... | 7·6 | 12·75 | 0·0485 | 30·79 | 32·0 | 160 | 200 |
| Lohys | 3·81 | 6·35 | 0·037 | 12·3 | 15·95 | 50 | 100 |

magnetic properties have been found by the Ballistic Galvanometer method, and the results are given in Table II. Figs. 1 and 2 show the various quantities plotted in terms of the maximum value of the magnetic induction B. The currents for the small magnetising forces were measured in terms of a Clark cell and standard resistance.

Lord Rayleigh found† by the magnetometer method that in the case of Swedish iron the values of the permeability μ corresponding to values of the magnetic force H varying from 0·00004 to 0·04 were very nearly constant. The curves obtained by plotting the values of μ and H in Table II tend to

* Mr. Hadfield states that the distinguishing feature of this alloy is that it contains about 3 per cent. of silicon.

† 'Phil. Mag.,' 1887.

become parallel with the axis of H as the values of H are diminished, and would predict limiting values of μ of 260 for Stalloy and 222 for Lohys.

Table II.

| B _{max.} | H _{max.} | Per. meability μ . | Coercive force H _c . | Residual magnetism B _r . | Ergs per cycle per cubic centimetre. | $\frac{[HdB]}{H_c B_{max.}}$ |
|-------------------|-------------------|------------------------------|------------------------------------|---|--|------------------------------|
| Stalloy. | | | | | | |
| 0·1267 | 0·000474 | 267 | — | — | — | — |
| 0·1918 | 0·000739 | 259·5 | — | — | — | — |
| 0·674 | 0·00267 | 252·5 | — | — | — | — |
| 0·937 | 0·00357 | 263 | 0·000056 | 0·015 | 0·0000111 | 2·68 |
| 1·870 | 0·00695 | 269 | 0·000126 | 0·040 | 0·0000672 | 3·58 |
| 3·60 | 0·01286 | 280 | 0·000382 | 0·10 | 0·000347 | 3·17 |
| 8·25 | 0·0251 | 329 | 0·0025 | 0·73 | 0·00384 | 2·34 |
| *13·02 | 0·0358 | 364 | 0·0045 | 1·50 | 0·01153 | 2·44 |
| 38·0 | 0·080 | 475 | 0·0095 | 5·00 | 0·0611 | 2·82 |
| 94·1 | 0·157 | 600 | 0·024 | 16·50 | 0·5680 | 3·12 |
| 171·0 | 0·245 | 698 | 0·040 | 31·0 | 1·686 | 3·06 |
| *269 | 0·312 | 862 | 0·080 | 71·5 | 4·810 | 2·81 |
| *629 | 0·420 | 1500 | 0·150 | 246·0 | 21·65 | 2·89 |
| 2245 | 0·677 | 3320 | 0·372 | 1473 | 203·0 | 3·06 |
| *8050 | 1·354 | 4470 | 0·60 | 4666 | 1030·0 | 3·58 |
| 8200 | 2·130 | 3850 | 0·67 | 6230 | 1688 | 3·86 |
| 9610 | 3·26 | 3020 | 0·73 | 7120 | 2335 | 4·11 |
| 11500 | 5·71 | 2020 | 0·75 | 7720 | 3110 | 4·54 |
| 13480 | 16·20 | 832 | 0·80 | 7970 | 4530 | 5·28 |
| Lohys. | | | | | | |
| 0·70 | 0·00311 | 225 | — | — | — | — |
| 1·95 | 0·0087 | 224 | — | — | — | — |
| 4·25 | 0·0181 | 235 | 0·000673 | 0·21 | 0·000725 | 3·18 |
| 8·99 | 0·0352 | 256 | 0·00296 | 0·69 | 0·00645 | 3·08 |
| 15·0 | 0·0628 | 284 | 0·00675 | 1·95 | 0·0224 | 2·78 |
| 37·4 | 0·1042 | 359 | 0·0188 | 7·00 | 0·152 | 2·72 |
| 84·1 | 0·1860 | 452 | 0·0445 | 20·30 | 0·84 | 2·82 |
| 286 | 0·404 | 709 | 0·133 | 103·0 | 8·80 | 2·92 |
| 568 | 0·565 | 1005 | 0·248 | 265 | 32·2 | 2·89 |
| 965 | 0·697 | 1385 | 0·368 | 550 | 83·0 | 2·94 |
| 1930 | 0·905 | 2135 | 0·535 | 1332 | 258 | 3·06 |
| 3780 | 1·260 | 3000 | 0·700 | 2959 | 725 | 3·45 |
| 6280 | 1·960 | 3210 | 0·835 | 5137 | 1620 | 3·89 |
| 7970 | 2·740 | 2910 | 0·920 | 6455 | 2375 | 4·08 |
| 11510 | 6·575 | 1757 | 1·12 | 8670 | 5060 | 4·90 |
| 13440 | 14·90 | 903 | 1·25 | 9360 | 7050 | 5·29 |

In fig. 2 curves of permeability are given for a very pure iron specimen* and a piece of transformer plate rolled from Swedish iron.† They show that the permeability of Stalloy is high for comparatively small values of the magnetic induction B, but rapidly diminishes as B is increased. The hysteresis loss for each of these specimens lies about midway between

* 'Roy. Soc. Proc.,' vol. 62, p. 371.

† 'Inst. Civ. Eng. Proc.,' vol. 126, p. 185.

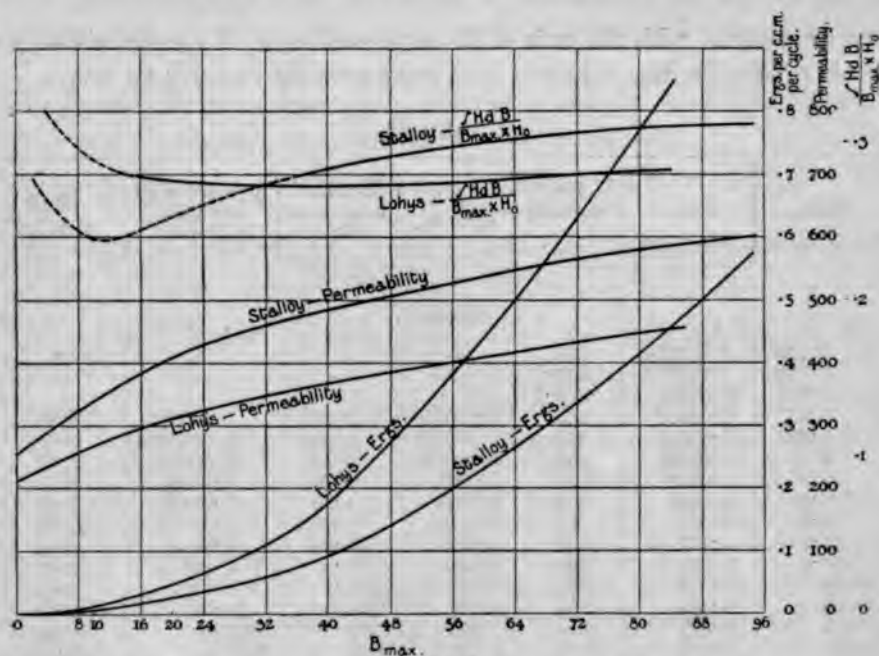


FIG. 1.

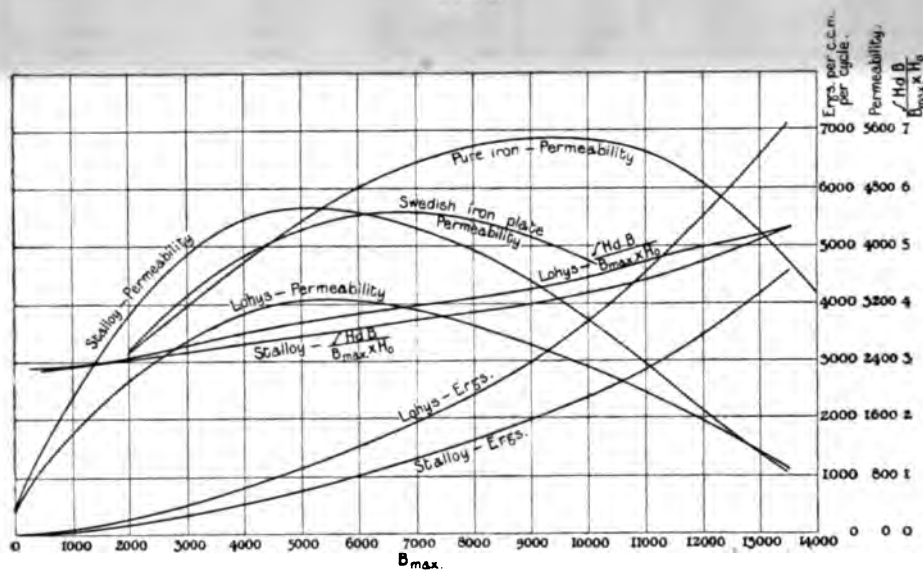


FIG. 2.

those for Stalloy and Lohys. It is interesting to note that the curves of permeability for values of the magnetic induction B varying from 15,000 to 22,000* continue the curves of permeability given in fig. 2, the change

* 'The Electrician,' October 18, 1907.

of the slope of the curve between the two being, however, somewhat abrupt in each case.

The Stalloy material requires careful attention in order that a truly symmetrical hysteresis loop may be obtained, more especially when the maximum induction B varies from about 200 to 8000. For instance, in an extreme case, after reducing the force H from about 63 to 0.712 without subjecting the specimen to a series of reversals of the magnetic force as it was reduced, a complete hysteresis loop was obtained. This loop is unsymmetrical in the sense that if the axis of H be so placed that the coercive forces are equal, the positive and negative values of the maximum induction B are not equal, but the positive and negative values of the residual magnetism B_0 are equal. Conversely, if the axis of H be so chosen that the total change of magnetism is halved, the values of the coercive forces are not equal, and the positive and negative values of B_0 differ from one another by 7 per cent. The value of the permeability, defined as the ratio of half the total change of magnetic induction to the maximum value of H , was less than was obtained when the loop was truly symmetrical. This effect persisted in spite of some hundreds of reversals of the magnetising force, and was only removed by re-applying the larger force and subjecting the specimen to magnetic reversals during the reduction of the magnetic force to the required value. In Table II the figures for loops which are not quite symmetrical are indicated by an asterisk.

A matter which has received further attention is the value of $\int H dB / H_0 B_{\max}$, where H_0 is the coercive force corresponding to the particular maximum value of the magnetic induction B . Dr. Sumpner* has pointed out that this quantity is accurately represented by a linear function of the maximum induction B over a large range. It will be seen from Table II and figs. 1 and 2 that this law ceases to hold for very small values of B .

The Steinmetz coefficients have been found between the values of the induction B mentioned in Table III, the law being Ergs per cubic centimetre per cycle $= \alpha B^\beta$. It will be seen that β varies between wide limits in the case of each of the materials.

The specific resistance and temperature coefficients were obtained from specimens 90 cm. long, 0.6 cm. broad, and 0.04 cm. thick by aid of the double bridge method, the specimen being submerged in an oil bath which was cooled by a mixture of ice and salt for the lower temperatures. The results are given in Table IV.

It is interesting to note that the eddy current loss calculated by aid of the

* 'Inst. Elec. Eng. Journ.,' vol. 36, p. 465.

Table III.

| Stalloy. | | | Lohys. | | |
|--------------|-----------|------------|-------------|-----------|------------|
| Range of B. | β . | α . | Range of B. | β . | α . |
| 0·937— 8·25 | 2·69 | 0·0000133 | 4·25— 37·4 | 2·46 | 0·0000207 |
| 8·25 — 94·1 | 2·05 | 0·0000505 | 37·4 — 568 | 1·97 | 0·000122 |
| 94·1 — 629 | 1·92 | 0·0000938 | 568 — 3780 | 1·64 | 0·000960 |
| 629 — 6050 | 1·71 | 0·000363 | 3780 — 7970 | 1·59 | 0·00148 |
| 6050 —11500 | 1·72 | 0·000321 | 7970 —13440 | 2·08 | 0·0000179 |
| 11500 —13480 | 2·37 | 0·00000752 | | | |

Table IV.

| Material. | Specimen. | Specific resistance at 15° C. in 10 ⁻⁶ ohm per cubic cm. | Mean temperature coefficient. | |
|---------------|------------|--|-------------------------------|---------------|
| | | | 0° C.—50° C. | 0° C.—100° C. |
| Stalloy | (1) | 49·05 | 0·00097 | 0·00101 |
| | (2) | 51·5 | — | — |
| | (3) | 48·35 | 0·00098 | 0·00105 |
| | Mean | 49·63 | 0·000975 | 0·00103 |
| Lohys..... | (1) | 13·96 | 0·00426 | 0·00451 |
| | (2) | 14·55 | 0·00422 | 0·00444 |
| | (3) | 14·25 | 0·00424 | 0·00444 |
| | Mean | 14·25 | 0·00424 | 0·00446 |

ordinary formula when added to the hysteresis loss gives a curve of total energy loss in close agreement with that published by the manufacturers. As would naturally be expected, the high specific resistance of Stalloy results in a very low eddy current loss.

The above experiments were carried out in the Siemens Electrical Engineering Laboratory, King's College, London.

*Note on the Representation of the Earth's Surface by Means of
Spherical Harmonics of the First Three Degrees.*

By A. E. H. LOVE, F.R.S.

(Received March 26,—Read April 30, 1908.)

In my paper on "The Gravitational Stability of the Earth,"* dynamical arguments were adduced in favour of the hypothesis that the distribution of density within the earth is such that the surfaces of equal density present, in addition to the inequalities depending upon the diurnal rotation, other inequalities which can be specified by spherical harmonics of the first, second, and third degrees. If this is the case, the surface of the earth, by which I mean the surface of the lithosphere, should present corresponding inequalities, and so also should the equipotential surfaces. Analytically, if the density ρ is given by an equation of the form

$$\rho = f_0(r) + \epsilon_1 f_1(r) S_1 + \epsilon_2 f_2(r) S_2 + \epsilon_3 f_3(r) S_3, \quad (1)$$

where $f_0(r), f_1(r), \dots$ are functions of the distance r from the centre, S_1, S_2, S_3 are spherical surface harmonics of degrees indicated by the suffixes, and $\epsilon_1, \epsilon_2, \epsilon_3$ are small coefficients, then the surface should have an equation of the form

$$r = a + \alpha_1 S_1 + \alpha_2 S_2 + \alpha_3 S_3, \quad (2)$$

where a and $\alpha_1, \alpha_2, \alpha_3$ are constants, and the α 's are small. The elevations and depressions of the lithosphere should be, at least in their main features, expressible by a formula of this type. The actual elevations and depressions are difficult to determine, because all that can be found by observation is the amount of elevation above, or depression below, a particular equipotential surface, the *geoid*, or the surface of the ocean, continued beneath the continents. For a first approximation the potential due to such a distribution of density as is expressed by (1) within a surface expressed by (2) would be given by formulæ of the type

$$V = F_0(r) + \beta_1 F_1(r) S_1 + \beta_2 F_2(r) S_2 + \beta_3 F_3(r) S_3, \quad (r < a),$$

$$V = F_0(a) \frac{a}{r} + \beta_1 F_1(a) \frac{a^2}{r^2} S_1 + \beta_2 F_2(a) \frac{a^3}{r^3} S_2 + \beta_3 F_3(a) \frac{a^4}{r^4} S_3, \quad (r > a),$$

where the β 's are small coefficients and the F 's are functions connected with the f 's by definite relations. Such formulæ would need correction in the immediate neighbourhood of the surface $r = a$, but there can be no doubt

* 'Phil. Trans.' (A), vol. 207 (1907), p. 171.

that the most important terms would be those containing harmonics of the same types S_1, S_2, S_3 as occur in the formula for τ . We should, therefore, expect that the shape of the earth, as expressed by the continental elevations and oceanic depressions, would be represented, at least in its main features, by a formula of the same type as (2). In my paper, cited above, I made a rough spherical harmonic analysis of these elevations and depressions. Denoting by θ the colatitude, measured from the North Pole, and by ϕ the longitude, measured eastwards from the meridian of Greenwich, I wrote, as the most general surface harmonic which contains no terms of degree higher than the third, the expression

$$\begin{aligned} & (p \cos \phi + q \sin \phi) \sin \theta + r \cos \theta \\ & + (\alpha \cos \phi + \beta \sin \phi) \sin 2\theta + (\gamma \cos 2\phi + \delta \sin 2\phi) \sin^2 \theta + \epsilon (3 \cos 2\theta + 1) \\ & + a (\cos 3\theta + 0.6 \cos \theta) + (b \cos \phi + c \sin \phi) (\sin \theta + 5 \sin 3\theta) \\ & + (d \cos 2\phi + e \sin 2\phi) (\cos \theta - \cos 3\theta) + (f \cos 3\phi + g \sin 3\phi) (3 \sin \theta - \sin 3\theta), \end{aligned} \quad (3)$$

and I found for the coefficients the values

$$\begin{aligned} p = 1161, \quad q = 824, \quad r = 1407, \quad \alpha = 593, \quad \beta = 661, \quad \gamma = -666, \quad \delta = -223, \\ \epsilon = 283, \quad a = -347, \quad b = -144, \quad c = 9, \quad d = -594, \quad e = 747, \\ f = 82, \quad g = 325. \end{aligned}$$

In these equations the ratios of the coefficients, not their absolute values, are representative of the computed elevations and depressions. The results were recorded in a chart (p. 237), concerning which I observed (p. 238) that its chief defects were the absence of any indication of an Arctic ocean and the almost complete submersion of South America. I stated also that there was no doubt that the coefficients could be adjusted to secure a better agreement with the geographical facts.

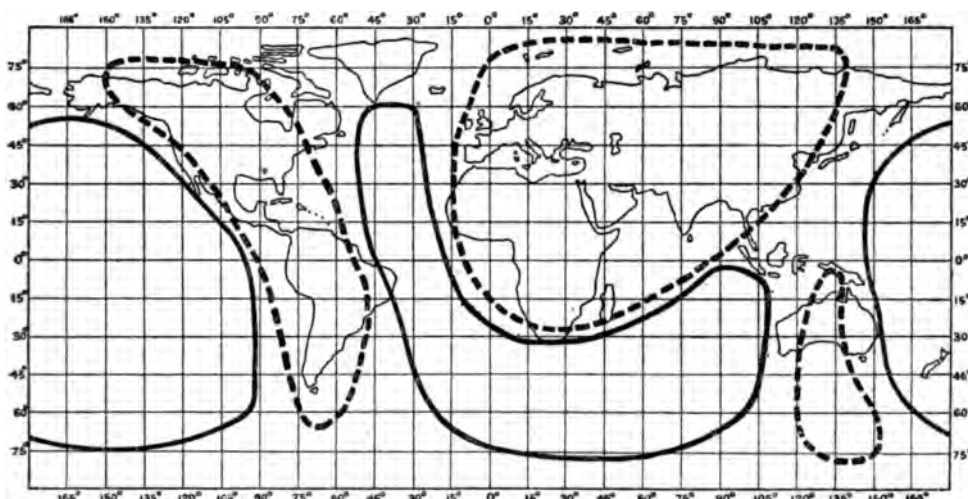
After a fresh computation of the coefficients, and a somewhat minute study of the elevations and depressions answering to each of the terms of (3), I have selected as the best of many tested sets of coefficients* the following:—

$$\begin{aligned} p = 16.5, \quad q = 9.5, \quad r = 8, \quad \alpha = 1.5, \quad \beta = 2.5, \quad \gamma = -7, \quad \delta = -4, \\ \epsilon = 1, \quad a = -5, \quad b = -1.25, \quad c = -0.5, \quad d = 0, \quad e = 6.5, \\ f = -0.25, \quad g = 3.5. \end{aligned}$$

The result is recorded in the annexed chart. The fine continuous line is a

* Adjustments of the coefficients to four digits are not desirable, as nothing more than a rough general agreement is sought. Some of the harmonic functions in formula (3) being capable of all values between something near to 5.5 and to -5.5, while others lie between ± 1 , a small difference in some coefficients, *e.g.*, b, c, f, g , has more influence on the result than a like difference in others, *e.g.*, p, a .

rough outline of the actual land of the globe, drawn in such a way that all degrees of latitude or of longitude have the same value on the map; the heavy line is the zero line of the surface harmonic with the coefficients here set down; the dotted line is the contour line along which the computed elevation is equal to one-tenth of its maximum value. The computed elevation is positive almost everywhere in the actual continents, and the zero line runs nearly everywhere in the neighbourhood of a line drawn between the contour lines of the surface of the earth at 1000 fathoms and 2000 fathoms depth.* The computed elevation is positive within the Arctic Ocean, as it should be, for that ocean belongs to the continental block but it is only moderate there. It is positive in South America, except the eastern extremity of Brazil, and the greater part of that continent is represented



as a region of superior elevation. Thus the two chief defects of the harmonic representation given in the paper above cited are not present in the new representation. In several other parts of the map the fitting of the actual shape is rather better now than it was before. The accord of the computed results and the geographical facts seem to be sufficiently good to warrant considerable confidence in the theory which led to the conclusion that harmonic inequalities of the first three degrees should be prominent.

[*Added, April 17, 1908.*—I take this opportunity of correcting an error in my paper, "The Gravitational Stability of the Earth," already cited. The

* Reference may be made to the bathymetric chart drawn, after Sir John Murray, in Chamberlin and Salisbury's 'Geology,' vol. 1, p. 10 (London, 1906), or to that drawn, after the Prince of Monaco, in É. Haug's 'Traité de Géologie,' vol. 1, p. 26 (Paris, 1907).

equation (109), p. 219, is deduced correctly from the system of equations of the type (108), and the forms given on pp. 219, 220 for the quantities ξ , W are deduced correctly from the equation (109), and the condition that the bounding surface is free from pressure; but the system of equations of the type (108) is not satisfied by these forms for ξ , W , and cannot be satisfied by any forms in which ξ , W are multiples of any surface harmonic. This result means that the state described in the paper as one of "lateral disturbance with a hemispherical distribution of density" cannot be maintained in a body devoid of rigidity and free from the action of external forces. It is not difficult to show that, in a body of finite rigidity, such a state can be a state of equilibrium; and that, when the initial state is, as in the paper, one of uniform density and hydrostatic pressure, the two chief features of the strained state are the same as those described in the paper. These features are (i) the formula for the excess density, represented graphically in fig. 1, p. 220, and (ii) the displacement of the surface of the body towards one side and the displacement of the equipotential surfaces towards the other side. The theory of § 50, pp. 221—224, must also be corrected in a similar way; but the correction does not affect the qualitative result that, when the rotation is taken into account, spherical harmonics of the third degree must be introduced.]

The Relation between the Crystalline Form and the Chemical Constitution of the Picryl Derivatives.

By GEORGE JERUSALEM and WILLIAM JACKSON POPE, F.R.S., Professor of Chemistry, Municipal School of Technology, Victoria University of Manchester.

(Received April 6,—Read April 30, 1908.)

The general relation existing between the constitution and the crystalline form of chemical substances has been determined by Barlow and Pope.* It is conveniently illustrated by assigning to each atom present a sphere or domain of influence, and constructing homogeneous close-packed assemblages corresponding in composition and constitution to the compounds concerned, using spheres as structural units to represent the spheres of atomic influence. On constructing such assemblages it is found that, for their dimensions to accord with the geometrical dimensions of the crystal, the spheres of influence, delimited by the polyhedral cells enclosed by tangent planes drawn through the points of contact of neighbouring spheres, must possess volumes approximately proportional to the fundamental valencies of the corresponding elements. The assemblages derived in this way exhibit properties corresponding with the chemical composition and constitution and with the crystalline form of the substance represented; they are found also to be homogeneously partitionable into units which correspond in configuration with the chemical properties of the substance.

The method of treatment here briefly indicated has been applied and tested to such an extent as proves its general applicability, and demonstrates that the principle involved is the correct one;† the conclusion that the fractions of the molecular volume appropriated by the component atoms are approximately proportional to the valencies of the respective elements has also been substantiated by independent work on the subject of molecular volumes.‡

As the theory indicates that the crystalline forms exhibited by related substances are derivable in a comparatively simple manner one from the other, it is desirable that groups of allied organic substances should be examined, as far as possible, by aid of the new method. We have, therefore, studied the whole of the crystallographic data available for the derivatives of the symmetrical radicle, picryl, namely, 1 : 3 : 5-trinitrophenyl, $C_6H_2(NO_2)_3$, and

* 'Trans. Chem. Soc.,' 1906, vol. 89, p. 1675; 1907, vol. 91, p. 1150.

† Jaeger, 'Trans. Chem. Soc.,' 1908, vol. 93, p. 517.

‡ Le Bas, 'Trans. Chem. Soc.,' 1907, vol. 91, p. 112; 'Phil. Mag.,' 1907, vol. 14, p. 324.

for purposes of comparison have determined experimentally the geometrical constants of several related substances.

Two distinct assemblages can be devised, both in accordance with the crystallographic and chemical data, to represent the crystal structure of benzene and its simple derivatives;* it has been shown that both these forms of assemblage can be traced among the simple derivatives of benzene. The first assemblage is derivable from the closest-packed assemblage of equal spheres of hexagonal type,† and, taking the volume of a monovalent sphere of atomic influence as unity, the dimensions of a unit of the partitioning of the assemblage, namely, of the benzene molecule itself, are determined by the following rectangular co-ordinates:—

$$x : y : z = 3.101 : 3.480 : 2.780.$$

These values constitute the so-called equivalence parameters for benzene and their product; the valency volume, $W = 30$, is the sum of the valencies of the atoms composing the benzene molecule, C_6H_6 .

The second form of assemblage met with among the simple derivatives of benzene is derived from the closest-packed assemblage of equal spheres of cubic type, and is therefore of rhombohedral marshalling; it differs dimensionally from the hexagonal type by exhibiting a smaller z value and a larger y value than the former.

From the papers referred to it appears that among the simple derivatives of benzene the dimension z varies less than do the other two, namely, x and y ; it would therefore seem that the adjustment of the assemblage which restores close-packing after the introduction of a substituting group into the benzene structure in general exerts itself mainly in the directions of x and y , and only affects but slightly the dimension z . The direction of z is that of the vertical dimension in the benzene molecule, that is to say, of the dimension perpendicular to the two planes containing the centres of the two sets of hydrogen atoms ordinarily numbered 1:3:5 and 2:4:6, respectively. It will be shown below that this approximate constancy of the vertical or z dimension is maintained in the more complex picryl derivatives.

Ammonium Picrate, $C_6H_2-1:3:5-(NO_2)_3-ONH_4$.

Ammonium picrate crystallises from water in orthorhombic forms; these have been measured by Handl‡ and by Laurent,§ who respectively assign to the substance the axial ratios:—

* 'Trans. Chem. Soc.,' 1906, vol. 89, p. 1692.

† *Loc. cit.*, p. 1699.

‡ 'Ber. k. Akad. Wien,' 1858, vol. 32, p. 259.

§ 'Revue Scient.,' vol. 9, p. 26.

$$a : b : c = 1 : 0.6787 : 0.3569$$

and

$$a : b : c = 1 : 0.6873 : 0.3652,$$

the mean values being $a : b : c = 1 : 0.6830 : 0.3611$.

Crystals much more suitable for exact measurement than these are obtained by crystallising the salt from acetone, in which it is fairly soluble; on allowing the acetone solution to evaporate spontaneously at the ordinary temperature, large transparent yellow crystals of hexagonal habit are deposited. The bright yellow colour of the crystals thus produced is quite distinct from the red tint sometimes assumed by ammonium picrate.* The forms $a\{100\}$ and $c\{001\}$ are generally the best developed, and $q\{021\}$ was only observed on one crystal; the following results were obtained on measurement:—

Crystal System. Orthorhombic.

$$a : b : c = 1.8914 : 1 : 1.3871.$$

Forms observed: $a\{100\}$, $c\{001\}$, $r\{201\}$, $q\{021\}$, and $o\{111\}$.

| Angle. | Number of observations. | Limits. | Mean. | Calculated. |
|--------------------|-------------------------|-----------------|-------------|-------------|
| 001 : 201 | 15 | 55° 33'—55° 56' | 55° 42' 50" | — |
| 100 : 111 | 12 | 66 34—66 53 | 66 47 10 | — |
| 001 : 111 | 20 | 57 21—57 58 | 57 32 20 | 57° 29' 30" |
| 111 : 11 $\bar{1}$ | 8 | 64 49—65 17 | 64 59 0 | 65 1 0 |
| 201 : 20 $\bar{1}$ | 5 | 68 21—68 58 | 68 35 40 | 68 34 10 |
| 201 : 111 | 9 | 50 56—51 20 | 51 5 30 | 51 3 50 |
| 111 : 021 | 4 | 27 45—27 51 | 27 47 0 | 27 55 10 |
| 001 : 021 | 2 | 70 17—70 22 | 70 19 30 | 70 10 40 |

The form $o\{111\}$ has not previously been observed on ammonium picrate crystals. The crystals exhibit a perfect cleavage on $a\{100\}$; this is also the optic axial plane, and the axis b is the acute bisectrix. The optic axial dispersion is very marked; the angle for red is much larger than that for yellow light.

The crystals deposited from water and from acetone are evidently of identical structure, for, on writing the axial ratios now given, namely,

$$a : b : c = 1.8914 : 1 : 1.3871,$$

in the form $a' : b' : c' = 1 : a/2c : 1/2c = 1 : 0.6818 : 0.3609,$

the result is practically identical with the mean of the measurements of Handl and Laurent, namely,

$$a : b : c = 1 : 0.6830 : 0.3611.$$

* Silberrad, 'Trans. Chem. Soc.,' 1908, vol. 93, p. 477.

On calculating the equivalence parameters of ammonium picrate from our determination of the axial ratios, taking the valency volume of the molecule, $C_6H_2(NO_2)_3ONH_4$, as $W = 56$, the following values are obtained:—

$$x : y : z = 5.251 : 2.776 : 3.582.$$

For comparison with these equivalence parameters it is convenient to calculate those of potassium picrate; this salt is orthorhombic with

$$a : b : c = 1.4352 : 1 : 1.0616,*$$

and by transposition the axial ratios may be obtained in the form

$$a : b : c = 2 : 1.0616 : 1.4352 = 1.8839 : 1 : 1.3519.$$

The latter values show clearly the isomorphism of this salt with the previous one; the equivalence parameters of potassium picrate, $C_6H_2(NO_2)_3OK$, with $W = 50$, are calculated from the last form of the axial ratios as

$$x : y : z = 5.082 : 2.699 : 3.647.$$

It is seen that on passing from the potassium to the ammonium salt the principal increase amongst the equivalence parameters occurs in the directions x and z , whilst the value of y changes to a smaller extent, namely, from 2.699 to 2.776. The dimension y in the cases of these salts obviously corresponds to the dimension $z = 2.780$ in benzene itself, and this dimension, as remarked above, is the one of the three which tends to change least on simple substitution.

Ammonium picrate has the same valency volume, $W = 56$, as the orthorhombic 1 : 3 : 5-trinitrobenzoic acid, $C_6H_2(NO_2)_3CO.OH$, with the axial ratios

$$a : b : c = 0.8770 : 1 : 0.5715,†$$

on interchanging in these axial ratios, c and b , b and a , and a and c , these values become

$$a : b : c = 1 : 0.5715 : 0.8770 = 1.7497 : 1 : 1.5346.$$

This set of axial ratios corresponds to the equivalence parameters

$$x : y : z = 4.816 : 2.753 : 4.224.$$

The y value again corresponds closely to that of ammonium picrate and to the z value of benzene, so that on replacing the group, ONH_4 , in the salt by the group, CO_2H , of the same valency volume, $W = 9$, the vertical benzene dimension is sensibly preserved.

The methyl ether of picric acid, 1 : 3 : 5-trinitroanisole, $C_6H_2(NO_2)_3OCH_3$,

* Brugnatelli, 'Zeitschr. Kryst. Min.,' 1895, vol. 24, p. 277.

† Friedländer, 'Zeitschr. Kryst. Min.,' 1877, vol. 1, p. 623.

also has the same constitution and valency volume, $W = 56$, as ammonium picrate; it crystallises in the monosymmetric system* with the axial ratios

$$a : b : c = 1.4635 : 1 : 2.2211, \beta = 50^\circ 48'.$$

These axial ratios may be transposed by assigning to the planes (100), (10 $\bar{1}$), and (110) the indices (10 $\bar{1}$), (001), and (11 $\bar{1}$), respectively, and then become

$$a : b : c = 1.7225 : 1 : 1.4635, \beta = 91^\circ 59'.$$

The equivalence parameters corresponding to these axial ratios are

$$x : y : z = 4.843 : 2.811 : 4.115, \beta = 91^\circ 59' \text{ or } 89^\circ 1'.$$

The y value is again approximately equal to the z value for benzene, and the substitution of the methoxyl group, .OCH_3 , for .ONH_2 or $\text{.CO}_2\text{H}$, has effected but little change in the dimensions of the crystal structure.

Picramide, $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{NH}_2$, which may be regarded as derived from ammonium picrate by the elimination of one molecule of water, crystallises in the monosymmetric system with†

$$a : b : c = 0.838 : 1 : 0.6638, \beta = 80^\circ 11'.$$

After dividing the length b by two, so that the axial ratios become

$$a : b : c = 1.676 : 1 : 1.3276, \beta = 80^\circ 11',$$

and calculating the equivalence parameters, taking the valency volume as $W = 52$, the following values are obtained:—

$$x : y : z = 4.815 : 2.873 : 3.814, \beta = 80^\circ 11'.$$

The y value differs rather more than before from the z value for benzene, but the z value is almost the same as for ammonium picrate.

The symmetrical trinitrotoluene, $\text{C}_6\text{H}_2\text{--}1:3:5\text{--}(\text{NO}_2)_3\text{--}6\text{--CH}_3$, has a valency volume two units less than that of ammonium picrate and trinitroanisole, namely, $W = 54$, and crystallises in the orthorhombic system with

$$a : b : c = 0.9373 : 1 : 0.6724.‡$$

On dividing the length b by two, as in the previous case, so as to obtain the axial ratios in the form

$$a : b : c = 1.8746 : 1 : 1.3448, .$$

and calculating the equivalence parameters, the following values are obtained:—

$$x : y : z = 5.206 : 2.777 : 3.735.$$

* Friedländer, 'Zeitschr. Kryst. Min.,' 1879, vol. 3, p. 173; compare Jaeger, *ibid.*, 1905, vol. 40, p. 565.

† Friedländer, *loc. cit.*

‡ Friedländer, *loc. cit.*

In this case both the x and y values are nearly identical with those for ammonium picrate, and the effect of the change of valency volume is thrown, in the main, upon the direction z .

Picryl chloride, $C_6H_2Cl-1:3:5-(NO_2)_3$, derived from picric acid by substituting chlorine for hydroxyl, has the valency volume $W = 48$, and crystallises in the monosymmetric system with

$$a : b : c = 1.83288 : 1 : 0.81135, \beta = 77^\circ 9'.$$

On transposing these axial ratios so that the planes (001), ($\bar{1}01$), (101), and (110) become respectively (103), ($\bar{1}01$), (301), and (110), the following values result:—

$$a : b : c = 1.7875 : 1 : 1.2175, \beta = 90^\circ 4'.$$

The corresponding equivalence parameters are

$$x : y : z = 5.013 : 2.804 : 3.414, \beta = 90^\circ 4' \text{ or } 89^\circ 56'.$$

The y dimension in this case also retains approximately its previous value.

Styphnic acid, $C_6H(OH)_2-1:3:5-(NO_2)_3$, the monohydroxy-derivative of picric acid, separates on spontaneous evaporation of its alcoholic solution in large straw-yellow prisms belonging to the hexagonal system; the following results were obtained on measurement:—

Crystalline System. Hexagonal.

$$a : c = 1 : 1.3890.$$

Forms observed: $\{10\bar{1}1\}$, $\{10\bar{1}0\}$, $\{11\bar{2}0\}$, and $\{0001\}$.

| Angle. | Number of observations. | Limits. | Mean. | Calculated. |
|---------------------------|-------------------------|------------------------------|---------------------|--------------------|
| $10\bar{1}1 : 01\bar{1}1$ | 8 | $50^\circ 17' - 50^\circ 3'$ | $50^\circ 12' 40''$ | — |
| $0001 : 01\bar{1}1$ | 15 | $57 45 - 58 25$ | $58 2 50$ | $58^\circ 3' 20''$ |
| $11\bar{2}0 : 01\bar{1}1$ | 6 | $42 37 - 43 5$ | $42 43 30$ | $42 42 10$ |
| $10\bar{1}0 : 10\bar{1}1$ | 5 | $31 42 - 32 5$ | $31 57 0$ | $31 56 40$ |

The first angle quoted, namely, $50^\circ 12' 40''$, has been given by Ditscheinert† as $50^\circ 12'$. On examining a section cut perpendicular to the principal axis, the uniaxial interference figure of the normal type is seen; the double refraction is strong and negative in sign. No indications were obtained of the hemimorphous development described by Lehmann.‡

For the purpose of comparing this substance with those discussed above,

* Bodewig, 'Zeitschr. Kryst. Min.,' 1879, vol. 3, p. 398.

† 'Annalen,' 1871, vol. 158, p. 247.

‡ 'Zeitschr. Kryst. Min.,' 1882, vol. 6, p. 51.

its crystal form is conveniently referred to an orthorhombic axial system, in which the new ratio

$$a' : b' : c' = a\sqrt{3} : a : c = 1.7321 : 1 : 1.3890.$$

The equivalence parameters of styphnic acid, for which $W = 52$, are thence calculated as

$$x : y : z = 4.825 : 2.786 : 3.869.$$

The y value is again practically identical with the z value for benzene.

The symmetrical trinitrophloroglucinol crystallises with water, the crystals having the composition, $C_6(OH)_3-1:3:5-(NO_2)_3, H_2O$, and belonging to the hexagonal system with

$$a : c = 1 : 1.0346.*$$

On increasing the length c by one-half and referring the axial ratios to an orthorhombic system of axes just as in the previous case, the axial ratios

$$a : b : c = 1.7231 : 1 : 1.5519$$

are obtained. The equivalence parameters calculated from these values, taking $W = 58$, are

$$x : y : z = 4.822 : 2.784 : 4.320.$$

The values for x and y are practically identical with those for styphnic acid, so that the morphotropic effect of introducing the group, OH, H_2O , in place of a hydrogen atom in the styphnic acid assemblage is merely to increase the dimension z . Cases of very similar character to this occur among the minerals of the humite series and between camphoric anhydride and the addition compound of camphoric acid with acetone.†

The above results show that, by applying the method given by Barlow and Pope to the crystallographic data, an extensive series of picryl derivatives can be at once referred in a very simple manner to the hexagonal assemblage described for benzene. The following picryl derivatives seem to be derived from the alternative benzene assemblage, that, namely, which possesses the rhombohedral type of marshalling.

The symmetrical trinitrobenzene, $1:3:5-C_6H_3(NO_2)_3$, is orthorhombic with the axial ratios‡

$$a : b : c = 0.9540 : 1 : 0.7330.$$

On dividing the length b by two, so as to obtain the axial ratios

$$a : b : c = 1.9080 : 1 : 1.4660,$$

* Ditscheiner, 'Zeitschr. Kryst. Min.,' 1881, vol. 5, p. 646.

† 'Trans. Chem. Soc.,' 1906, vol. 89, p. 1685.

‡ Friedländer, *loc. cit.*, p. 170.

and calculating the equivalence parameters, with $W = 48$, the following values result:—

$$x : y : z = 4.921 : 2.579 : 3.781.$$

The y value is in this case much smaller than among the previously discussed substances.

The 1:3:5-trinitrobenzene is identical in constitution and valency volume with the tribromo-1:3-dinitro-5-methylbenzene, and the two substances are morphotropically very closely related; the latter is monosymmetric with*

$$a : b : c = 0.5217 : 1 : 0.7803, \beta = 85^\circ 12'.$$

On interchanging the axial directions a and b , the axial ratios are obtained in the form

$$a : b : c = 1.9168 : 1 : 1.4957, \alpha = 85^\circ 12'.$$

These values correspond to the equivalence parameters

$$x : y : z = 4.909 : 2.561 : 3.831, \alpha = 85^\circ 12'.$$

The above numbers show that in the passage from the symmetrical trinitrobenzene to the dinitrotribromotoluene of similar constitution, which results from replacing one nitro-group in the former by a methyl-group of the same valency volume, and replacing three hydrogen atoms by three bromine atoms, also of the same valency, practically no change is effected in the relative dimensions; the equivalence parameters are scarcely affected by the substitution.

It has been already remarked that the differences in dimensions between the benzene assemblages of hexagonal and of rhombohedral marshalling are greatest in the directions of y and z , so that the dimension x remains nearly the same in both. A similar correspondence would be expected to hold among the derivatives of benzene, and accordingly it is found that the x values, 4.909 and 4.921, of the dinitrotribromotoluene and the trinitrobenzene respectively, are nearly identical with the x value, 5.013, of picryl chloride, the three substances having the same valency volume.

These correspondences strongly indicate that the above two substances exhibit in their crystalline structure the second form of the benzene assemblage; the same conclusion presumably holds for picric acid and picryl iodide, both of which crystallise in pseudo-cubic forms.

Picric acid crystallises in the orthorhombic system with

$$a : b : c = 1.0305 : 1 : 1.0434, \dagger$$

and has the valency volume $W = 50$. The equivalence parameters are

$$x : y : z = 3.706 : 3.596 : 3.752.$$

* Jaeger, 'Zeitschr. Kryst. Min.', 1905, vol. 40, p. 360.

† Brugnatelli, 'Zeitschr. Kryst. Min.', 1895, vol. 24, p. 277.

Picryl iodide, $C_6H_2I-1:3:5-(NO_2)_3$, with $W = 48$, crystallises in the tetragonal system with

$$a : c = 1 : 1.958.*$$

On halving the length c , and writing the axial ratios in orthorhombic form, the equivalence parameters are obtained as

$$x : y : z = 3.660 : 3.583 : 3.660.$$

These values approximate very closely to those obtained for picric acid, and indicate that the replacement of iodine in picryl iodide by hydroxyl, to yield picric acid, results in the corresponding assemblage being slightly expanded in all directions, in accordance with the second geometrical property described by Barlow and Pope.†

The equivalence parameters determined in the previous pages are collected in the following table.

| Substance. | $x : y : z$ | β . | W. | Crystal system. |
|---|-----------------------|-------------------------|----|-----------------|
| Substances of Hexagonal Marshalling. | | | | |
| C_6H_6 ($y : z : x$) | 3.480 : 2.780 : 3.101 | 90° | 30 | Orthorhombic. |
| 1 : 3 : 5- $C_6H_2(NO_2)_3ONH_4$... | 5.251 : 2.776 : 3.852 | 90° | 56 | " |
| 1 : 3 : 5- $C_6H_2(NO_2)_3OK$ | 5.082 : 2.699 : 3.647 | 90° | 50 | " |
| 1 : 3 : 5- $C_6H_2(NO_2)_3CO_2H$... | 4.816 : 2.763 : 4.334 | 90° | 56 | " |
| 1 : 3 : 5- $C_6H_2(NO_2)_3OCH_3$... | 4.843 : 2.811 : 4.115 | 89° 1' | 56 | Monosymmetric. |
| 1 : 3 : 5- $C_6H_2(NO_2)_3NH_2$... | 4.815 : 2.873 : 3.814 | 80° 11' | 52 | " |
| 1 : 3 : 5- $C_6H_2(NO_2)_3CH_3$ | 5.206 : 2.777 : 3.735 | 90° | 54 | Orthorhombic. |
| 1 : 3 : 5- $C_6H_2(NO_2)_3Cl$ | 5.013 : 2.804 : 3.414 | 89° 56' | 48 | Monosymmetric. |
| 1 : 3 : 5- $C_6H(NO_2)_3(OH)_2$... | 4.825 : 2.786 : 3.869 | 90° | 52 | Hexagonal. |
| 1 : 3 : 5- $(NO_2)_3C_6(OH)_3H_2O$ | 4.822 : 2.784 : 4.820 | 90° | 58 | " |
| Substances of Rhombohedral Marshalling. | | | | |
| 1 : 3 : 5- $C_6H_2(NO_2)_3$ | 4.921 : 2.579 : 3.781 | 90° | 48 | Orthorhombic. |
| 1 : 3 : 5- $C_6Br_3(NO_2)_2CH_3$... | 4.909 : 2.561 : 3.831 | $\alpha = 85^\circ 12'$ | 48 | Monosymmetric. |
| 1 : 3 : 5- $C_6H_2(NO_2)_3OH$ | 3.706 : 3.596 : 3.572 | 90° | 50 | Orthorhombic. |
| 1 : 3 : 5- $C_6H_2(NO_2)_3I$ | 3.660 : 3.583 : 3.660 | 90° | 48 | Tetragonal. |

An inspection of the equivalence parameters of those picryl derivatives which assume the hexagonal type of marshalling shows, as previously noted, that the substitution in the benzene assemblage occurs so that groups which enter the benzene assemblage as substituting radicles are accommodated as the result mainly of an expansion of the assemblage in the directions of x and y ; the z dimension of benzene can thus be distinctly traced throughout the series of picryl derivatives as the y dimension of the latter. This conclu-

* Fels, 'Zeitschr. Kryst. Min.,' 1900, vol. 32, p. 364.

† 'Trans. Chem. Soc.,' 1907, vol. 91, p. 1204.

sion indicates that the columns, consisting of superposed layers of three triangularly arranged carbon spheres, which form the skeleton of the crystalline benzene assemblage,* exist in all these crystalline substances, and that the corresponding assemblages are derived by pushing these columns apart and packing the substituting groups into the space thus provided. The equivalence parameters now given furnish the data requisite to the construction of diagrams similar to those previously given by Barlow and Pope, which show the precise mutual arrangement of the constituents of the substituting radicles in the picryl derivatives.

If the conclusion drawn concerning the existence of the columns of carbon spheres in these assemblages is of general application, it should be possible to detect the z dimension for benzene throughout all the benzene derivatives of hexagonal marshalling.

No difficulty appears to exist in applying the method of treatment used in this paper to the more complex picryl derivatives. Thus, acetamide picrate, $\text{CH}_3\text{CO.NH}_2$, $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$, crystallises in the orthorhombic system† with

$$a : b : c = 0.4849 : 1 : 0.3544.$$

The valency volume, $W = 68$, and the corresponding equivalence parameters are

$$x : y : z = 3.560 : 7.342 : 2.602.$$

Further, isoapiol picrate, $\text{C}_{12}\text{H}_{14}\text{O}_4$, $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$, crystallises in the monosymmetric system‡ with

$$a : b : c = 0.9163 : 1 : 0.4226, \beta = 89^\circ 55'.$$

The valency volume, $W = 120$, and the corresponding equivalence parameters are

$$x : y : z = 6.201 : 6.767 : 2.860, \beta = 89^\circ 55'.$$

In each of these cases one of the three equivalence parameters has a value not greatly different from the value, $z = 2.780$, for benzene; this would be expected if the columns of carbon spheres present in the benzene assemblage remain intact in these compounds.

* 'Trans. Chem. Soc.,' 1906, vol. 89, p. 1695.

† Wyrouboff, 'Ann. Chim. Phys.,' 1895 (7), vol. 5, p. 99.

‡ Boeris, 'Zeitschr. Kryst. Min.,' 1905, vol. 40, p. 106.

*A Photographic Determination of the Elements of the Orbits
of Jupiter's Satellites.*

By BRYAN COOKSON, M.A., Mackinnon Student, July, 1904—July, 1906.

(Communicated by H. F. Newall, F.R.S. Received April 13,—Read
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During the opposition of Jupiter in 1902, the writer, by Sir David Gill's kind permission, was engaged in making a series of measurements of the relative positions of the four Galilean satellites with the 7-inch heliometer at the Cape Observatory. Simultaneously with these visual observations, photographs were taken with the astrographic telescope. This paper contains a short account of the work done in connection with the photographs; a detailed account has appeared as vol. 12, part IV, of the 'Annals of the Cape Observatory.'

The theory of the motions of Jupiter's satellites is one of the most interesting in celestial mechanics, and in order to test the existence of some remarkable theoretical inequalities, it is necessary to possess an accurate knowledge of the elements of the orbits. At the present time we do not possess this knowledge and it was with a view of contributing towards its attainment that the writer undertook these investigations.

The investigation with the heliometer was undertaken with the object of determining the mass of Jupiter and correcting the best available elements of the orbits of the satellites, which observation showed were considerably in error. The object in view in taking the photographs was to compare the visual and photographic methods and to see whether the much less laborious and more convenient methods of photography would yield results of the same high order of accuracy as the heliometer.

The number of photographs which were measured and discussed is 35. The measurement of them was carried out at the Cape in duplicate by Mr. Löwinger and the writer, the measuring micrometer being one of those used for measuring the plates of the astrographic catalogue. Nearly all the reductions were made by the writer after his return to England from the Cape. Owing to the special nature of the photographs, the usual method of determining the plate constants could not be employed. The usual procedure is to determine the three constants of plate-centre, scale-value, and orientation from measurements of three or more stars whose meridian places are known. In the present case this method was impracticable because the brightness of the satellites made it necessary to cut down

the aperture of the object-glass ; with the reduced aperture none but bright stars could be photographed in the same field with the planet, and of these there were not enough. But the same two standard stars as were used in the heliometer investigation were bright enough to leave measurable images on the plate, and from them two of the constants, namely, scale-value and orientation (referred to the earth's mean equator of 1902), were determined for every plate. The orientation was also determined independently from measurements of the trail of one of the satellites.

It was important that the orientation should be determined with special care, for on it depend the values found for the inclinations and nodes of the orbits of the satellites. The remaining constant, viz. the plate centre, did not enter, for the quantities which were to be given by measurement were the differences between the co-ordinates of Jupiter's centre and the centres of the satellites. Thus the measured co-ordinate of a satellite referred to Jupiter's centre as origin and corrected for scale-value, orientation, and refraction, is its co-ordinate referred to axes parallel and perpendicular to a plane parallel to the earth's mean equator of 1902 and passing through Jupiter's centre. The uncertainty in the measurement of the position of Jupiter's centre, which arose from the ill-defined image of the planet's disc on the photographic plate, was eliminated by a process of successive approximation, which will be explained presently. The theory with which the observations were compared was that of Souillart. Marth's Tables, which are based upon this theory and were published in the 'Monthly Notices Roy. Astr. Soc.,' vol. 51, were used, with certain corrections, for calculating the values of the longitudes and radius vectors. The calculated co-ordinates were rectangular co-ordinates referred to axes parallel and perpendicular to Jupiter's equator, the origin being at the planet's centre. By the choice of the equator of Jupiter instead of the earth's as plane of reference, this part of the work was much simplified.

In order to simplify the numerical work still further, the axes of reference for the measured co-ordinates were rotated into parallelism with axes parallel to Jupiter's equator.

Corrections were sought to all the elements of the orbits excepting the mean motions, which could only be determined by a series of observations extending over a much greater period of time than that covered by the present series.

Corrections were also sought to the coefficients of the "Great Inequalities" in the motions of the three inner satellites, inequalities which arise from the near commensurability of their mean motions. Since the equations for the four satellites had no unknown quantity in common, the four sets of

equations could be solved separately. The values of the unknowns were found by the method of least squares, and were substituted in the original equations of condition. If, now, an error had been made in measuring the position of the centre of Jupiter's disc on any given plate, this error would be common to the measurements of all four satellites on that plate, and would appear as a residual common to the four equations derived from that plate.

Accordingly, the mean residual for every plate was found and was applied as a correction to the measured co-ordinates of the four satellites. Thus corrected the equations were solved again. In this way a second approximation to the values of the unknowns was arrived at. The mean residuals from this second approximation were now all so small as to have no practical significance, and the second approximation to the values of the unknowns was taken as final. The agreement between these values and those found from the heliometer investigation was satisfactory; many of the unknowns did not differ by more than their probable errors, and the numerical results are in general the same.

In point of accuracy, as measured by interagreement of the observations, the photographic method is more accurate than the heliometric. The probable error of a visual observation of weight unity was about $\pm 0''.095$, whereas that of a photographic observation was $\pm 0''.061$. Moreover, it may be pointed out that the measurements of the photographs were not made on a measuring micrometer designed to attain the highest accuracy; a more elaborate measurement might have given even better results. On the other hand, for this particular class of visual observations the heliometer is the most refined instrument known, but, nevertheless, the probable error of one observation of a large series has not yet been brought below $\pm 0''.080$. Thus, in point of accuracy, the photographic method is superior to the heliometer. But perhaps the heliometer is superior in its more probable freedom from systematic error; in measurements of absolute angular distances the heliometer is to be preferred chiefly on account of the difficulty of determining the optical distortion of a photographic lens.

A knowledge of the mass of a planet attended by satellites is arrived at by observation of their times of revolution and of their mean distances from the planet. It is necessary that observation should provide the values of the mean distances expressed in absolute angular measure, and for this purpose the heliometer is the most suitable instrument, provided the satellites are bright enough.

The mass of the system of Jupiter, in terms of the sun's mass, was determined with great care from the heliometer observations. The value finally deduced is

$$1 : 1047.30 \pm 0.06.$$

As to the methods of reduction, the photographic is much the less laborious of the two, an advantage which arises chiefly from the use of rectangular co-ordinates referred to conveniently chosen axes. At some future date it will be necessary, in order to find the values of the secular variations of the elements, to reobserve the positions of the satellites, and there can be little doubt that the best and most convenient method of making the observations will be the photographic method.

One of the most remarkable of Laplace's theoretical discoveries was that the well-known relation between the longitudes of the first three satellites oscillated about a mean position, that is, when expressed analytically,

$$\epsilon_1 - 3\epsilon_2 + 2\epsilon_3 = 180^\circ - D \sin(bt + E),$$

where D and E are two constants of integration and b can be regarded as a known function of the masses of the three satellites of the form

$$(Am_1m_2 + Bm_2m_3 + Cm_3m_1)^{\frac{1}{2}}.$$

This periodic term was called by Laplace the libration.

Once the masses are known, the period becomes known, but D and E must be determined by observation. Eclipse observations failed to show E , and the reason given was that E was too small to be detected by observation. But the more probable reason is that, since the necessary eclipse observations extend over a considerable period of time, they must be combined by assuming the period $2\pi/b$ to be known; if the period is not known, or if a wrong value is assigned to it, the coefficient D cannot be found. Since the period is a function of the masses, the masses must be known before eclipse observations can be expected to reveal the value of the coefficient. But values of the masses are still very doubtful: the masses of satellites II and III are fairly well known to within 4 or 5 per cent., but the masses of both I and IV are doubtful to the extent of 50 per cent., and the period of the libration varies according to the values adopted from 4.5 to 6.2 years. Hence, eclipse observations cannot be expected to disclose the value of Laplace's libration. The values of $\epsilon_1, \epsilon_2, \epsilon_3$ can, however, be determined with great weight by heliometric or photographic observations extending over only three or four months. Hence the heliometer or photographic telescope may succeed where eclipse observations have failed. The values of $\epsilon_1 - 3\epsilon_2 + 2\epsilon_3$ found by the writer are as follows:—

| | |
|--|--|
| With heliometer at epoch 1901.61 | $\epsilon_1 - 3\epsilon_2 + 2\epsilon_3 = 180^\circ + 0^\circ 002 \pm 0^\circ 023$ |
| With heliometer at epoch 1902.60 | $180^\circ + 0^\circ 164 \pm 0^\circ 017$ |
| With photographs at epoch 1902.60 ... | $180^\circ + 0^\circ 202 \pm 0^\circ 017$ |

But it is not yet safe to conclude that the whole of this is due to Laplace's

libration: we must first be satisfied that the quantities ϵ_1 , ϵ_2 , ϵ_3 do truly represent mean longitudes and that they include no erroneous or unknown inequalities in longitude. This would entail a thorough revision of the whole theory of the satellites. Observation, then, is in advance of theory, and interesting questions cannot be settled until theory is revised and further elaborated.

Helimetric and photographic measurements are of more value than photometric measurements of eclipses in determining the positions of the satellites' orbits. The nodes and inclinations of the orbits are determined by the duration of eclipses, and an observation of the duration of an eclipse is liable to considerable error. But with the heliometer or photographic telescope the position of the orbit is given by measurement of position-angle or its equivalent in rectangular co-ordinates; and it is clear that measurements of the position-angle or rectangular co-ordinates of a satellite at its greatest elongation will provide more reliable information concerning the position of the orbit than the duration of eclipses.

The quantity which it is of most interest to determine is the motion of the node of the second satellite measured on Jupiter's equator. Hence, it is of importance to find from observation the position of the orbit at epochs at considerable intervals. It is well known that the effect of an equatorial protuberance of the primary is to cause a retrograde motion of the node of a satellite's orbit along the equator of the primary: the inclination remains constant, so that the pole of the satellite's orbit describes a small circle round the pole of the equator of the primary. The following table shows the percentage of the motion of the nodes which is due to the compression of Jupiter and the disturbing effect of the other satellites:—

| Satellite. | Yearly motion. | Compression of Jupiter. | I. | II. | III. | IV |
|------------|----------------|----------------------------|-----------|-----------|-----------|-----------|
| | ° | per cent. | per cent. | per cent. | per cent. | per cent. |
| I | 51.5 | 97 | — | 2 | 1 | 0 |
| II | 12.0 | 82 | 4 | — | 13 | 1 |
| III | 2.6 | 75 | 2 | 13 | — | 9 |
| IV | 0.74 | 36 | 1 | 3 | 48 | — |

Thus in the case of the second satellite which has an orbit at an inclination of $0^{\circ}.48$ to Jupiter's equator, the node retrogrades 12° per annum, and of this motion 82 per cent. is due to the compression of Jupiter, 4 to the influence of satellite I, 13 to that of III, and 1 to that of IV. The orbits of satellites I and III have only small inclinations to the planet's equator, and are, therefore, not suitable for measuring the motion of the

nodes. But the motion of the node of II can be measured, and affords the best means of finding the physical compression of Jupiter.

The fifth satellite discovered by Barnard is so near to the primary that the node of its orbit revolves through about 912° per annum, and second order terms begin to make themselves felt. A careful measurement of this motion would be of much value, for a comparison of the compression of Jupiter, deduced from the motion of the node of V with that deduced from the motion of the node of II, might provide information concerning the distribution of mass in Jupiter.

Helium and Radio-activity in Rare and Common Minerals.

By the Hon. R. J. STRUTT, F.R.S.

(Received April 23,—Read May 7, 1908.)

CONTENTS.

| | PAGE |
|---|------|
| § 1. Introduction..... | 572 |
| § 2. Experimental Methods | 575 |
| § 3. Statement of Experimental Results | 578 |
| § 4. Helium and Radio-activity of Ordinary Elements | 591 |
| § 5. Presence of Argon and Neon in Minerals | 592 |
| § 6. Summary of Conclusions | 594 |

§ 1. *Introduction.*

The original discovery of helium in cleveite and other minerals by Ramsay, and the subsequent explanation of its presence as due to production *in situ* by radio-active change, are of fundamental importance, and are too well known to need anything more than mention here. No exception has been known hitherto to the rule that helium is found in radio-active minerals exclusively—minerals, that is, in which either uranium, or thorium, or both, are present in appreciable quantity.

It seemed, however, that valuable information might be gleaned from a fuller examination of the subject than has yet been made.

In the first place, Rutherford has suggested with great plausibility that subatomic changes might be going on in some of the ordinary elements with emission of α particles of somewhat lower velocity than those of the radio-active elements. In such cases, owing to the abrupt disappearance of ionising and photographic action below the critical velocity, the activity

would not make itself apparent by ordinary experimental tests. If, however, helium were a product of such a change, we might expect to find it stored up in minerals containing the element in question.

Again, as many observers have found, ionising radiation is given off by the ordinary elements. It has been supposed (and I was myself one of the first to urge that view) that this ionising radiation indicated a feeble radio-activity. The progress of knowledge has made this more doubtful than it seemed at first. One strong objection is derived from a consideration of the internal heat of the earth.* Another is derived from the want of satisfactory constancy in the amount of this ionising radiation from different samples of a metal.† It seemed that the investigation proposed might give evidence as to whether or not this ionising radiation resembled genuine radio-activity in being associated with a production of helium.

The further object was proposed of looking for argon and the other inert gases in minerals. In view of the well-known experiments of Ramsay and Cameron,‡ it is unnecessary to emphasise the interest of this question.

The result of the experiments has been that helium is found to be a nearly universal constituent of minerals, when sufficiently refined methods of isolating it are adopted. With regard to argon it is much more difficult to pronounce. The spectrum, it is true, was in nearly all cases observed.

Where the total inert residue (argon with helium) was small, the argon found was not infrequently the greater part. However, in these cases the actual quantity of argon did not usually much exceed a cubic millimetre, a quantity which would be accounted for by contamination with 1/10 c.c. of air. It is not easy to carry out the complicated manipulations involved with complete certainty of excluding this amount of leakage. However, in the case of a few minerals, much less argon than this was observed, so that such leakage is not inevitable. I do not doubt that by careful working and with many repetitions the question of whether argon is commonly present in minerals to the extent of 1 cubic millimetre per kilogramme could be settled. In the case of igneous rocks it certainly *is* present in larger quantities than this, and I believe that the same is true of certain other siliceous materials, but further examination is required.

In the case of helium, no uncertainty of this kind is encountered. For it is only present in the air in infinitesimal proportions.

In determining whether or not the helium present in a mineral can be attributed to traces of the radio-active elements, I apply, in the first place, the

* 'Nature,' December 21, 1905.

† 'Phil. Mag.,' June, 1903. Also MacLennan, 'Phil. Mag.,' [6], vol. 14, p. 760, 1907.

‡ 'Chem. Soc. Proc.,' vol. 91, p. 1593, 1907.

crude test of comparison with the strongly radio-active minerals, in which helium is certainly derived from that source. If the quantity of helium should not be greater relatively to the radium than in such minerals, there is no *primâ facie* reason to look further for its origin. The radium in a mineral is proportional to the uranium contained in it, and, when known, allows the latter to be calculated. Both, in all probability, contribute to the helium present, and a more convenient unit is obtained by computing the volume of helium per gramme of uranium oxide than by expressing it relatively to the radium content. I shall call this, for brevity, the helium ratio.

Many of the strongly active minerals contain thorium, which also contributes to the helium contained.* In such cases, the ratio of helium to uranium may be much higher than in those where the uranium series is of chief importance. In establishing the normal helium ratio I shall ignore the former class.

It would scarcely be feasible to determine the probably very minute amount of thorium in the common minerals and ores; but it will appear in the sequel that the results of the present paper are not, as it happens, rendered difficult of interpretation by this circumstance.

The amount of helium found in the minerals will, of course, depend on the time which has elapsed since their formation, and is accordingly limited by the geological age of the strata in which they occur. It is unfortunate that geological evidence as to the age of metalliferous veins is usually vague; nor can it even be regarded as certain that all the minerals in the same vein are approximately contemporary. Further, we cannot be sure that all the helium which has been generated in the minerals still remains there. A part may have escaped. For these reasons the present investigation has no claim to be regarded as strictly quantitative. Nearly all the minerals examined occur in palæozoic rocks, and, except in a few extreme cases, I shall not attempt to distinguish the geologically older minerals from the geologically younger ones. The object of the investigation is to test materials of widely diverse chemical nature. To attain this it is necessary to be content with but vague information as to their geological age. Nevertheless, the general result will, I think, be regarded as fairly clear when the data given in this paper are examined.

The very interesting problem of tracing the effect of geological age on the helium ratio must be left for future treatment. Such materials as limestones suggest themselves as suitable for this investigation.

* 'Roy. Soc. Proc.' A, vol. 80, p. 56.

§ 2. *Experimental Methods.*

To extract helium from a mineral, we have the choice of two methods. The gas may be extracted by chemical disintegration of the material, or by heat. In the present case it was desired to look for helium present in very minute proportions, and to do this adequately it was necessary to extract the gas from large quantities of material, in some cases as much as 1 kilogramme or even more. It is scarcely feasible to decompose chemically such quantities of refractory minerals, when the onerous condition of working in a perfectly air-tight apparatus has to be observed. I have, therefore, contented myself with the summary method of heating the minerals to redness. It is true that the whole of the helium is not liberated in this way, but, for a pioneering investigation like the present, it was considered sufficient to assume that the quantity extracted by heat was half the total, as in the case of cleveite and kindred minerals.*

When less than 200 grammes of the mineral was to be heated, tubes of hard glass were used. For larger quantities it was found convenient to use weldless steel tubing, such as is used for building the frames of bicycles and motor cars. The tube was closed at one end with a cap turned out of rolled brass and soldered on to the steel with silver solder.† The steel tube was heated either in a gas furnace or, what is better, by electrical means. In the latter case the tube was wrapped in asbestos paper, and over this was wound a helix of nickel wire, through which the heating current could be passed. Over this was a thick layer of asbestos for heat insulation.

A glass exit tube was connected to the steel tube by means of a rubber cork, which was jacketed externally with water. This jacket served the double purpose of preventing any inward leakage of air under exhaustion and of protecting the rubber from injury by heat conducted along the hot metal.

The powdered mineral was placed in the steel tube, which was exhausted by a mercury pump. After it had stood exhausted all night, a little oxygen was added, and removed by the pump, so as to wash out all traces of air. Heat was then applied to drive off the gases contained. These gases passed over potash, then hot copper oxide, then over potash again, finally over phosphoric anhydride. These reagents absorbed most of the hydrogen and oxides of carbon evolved. The gas which passed them was collected through

* Travers, 'Roy. Soc. Proc.', vol. 64, p. 141, 1898.

† It is found much easier in practice to close the tube air-tight with a cap than with a plug.

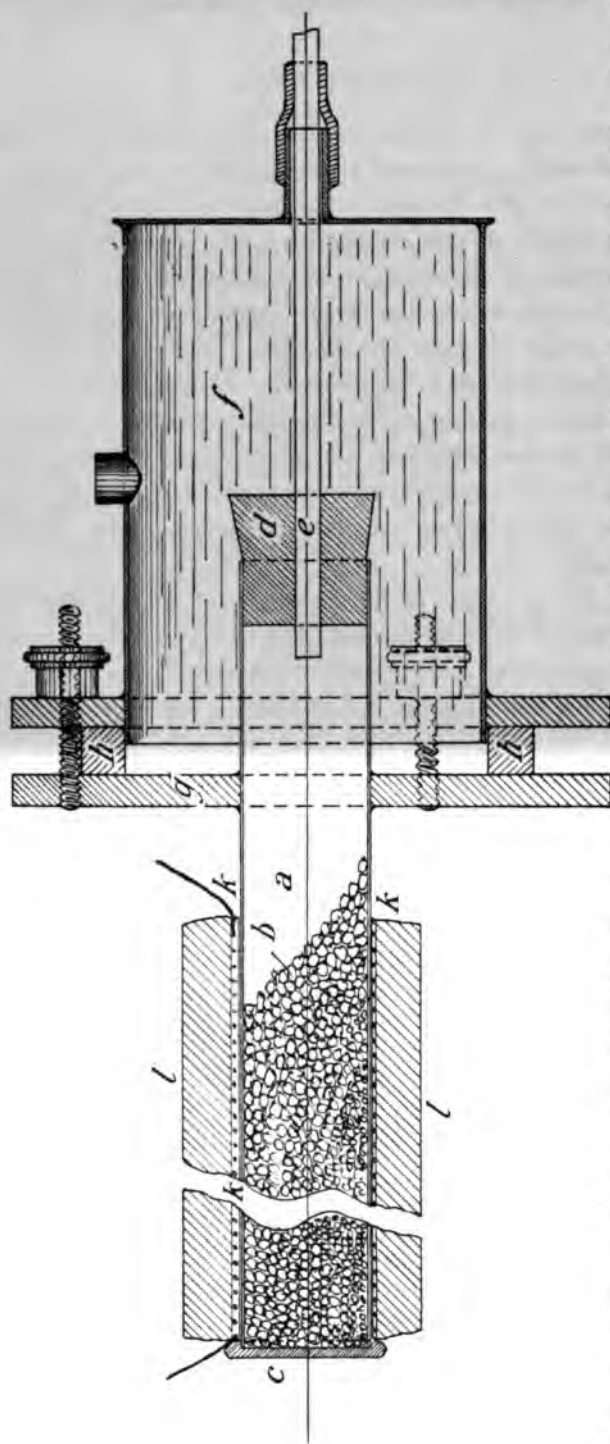


FIG. 1.—Retort used for extracting gases from minerals by heat. *a*, Weldless steel tube-containing the powdered mineral *b*, and closed air-tight at one end by the brass cap *c*, hard soldered on, and at other end by rubber cork *d*; *e*, glass tube for extraction of gas; *f*, water-jacket closed by the plate *g*, soldered on to *a*. The joint is made water-tight by the rubber ring *hh*. The retort is heated by the resistance coil *kk*, of nickel wire, insulated by asbestos paper, and surrounded by the asbestos jacket *ll*.

the pump. When the tube had been kept at a full red heat for two hours,* practically nothing more could be extracted.

The gas thus collected consisted chiefly of nitrogen, which exists in nearly all the minerals examined. To remove this nitrogen, sparking with oxygen was resorted to. The operation was carried out over mercury, in a eudiometer with wires sealed in at the top, which very nearly touched one another. A fragment of solid potash, partially hydrated, floated on the top of the mercury. The spark, or rather arc, was produced by a Ruhmkorff coil with an alternating current in the primary. The electrodes being fixed, the arc cannot be conveniently started by approximating them. The starting was effected by allowing the hammer of the coil to vibrate in synchronism with the supply, which it readily did, producing a spark, as when a battery is in use. The spark soon degenerated into an arc, and the hammer then ceased to vibrate. The primary current was promptly diminished by resistance, so that the arc should not be large enough to risk melting the electrodes or cracking the glass. Oxidation and removal of nitrogen then proceeded without attention. It is much better not to hurry the process by increasing the current. With a small arc there is little danger of any accident involving loss of the gas. After contraction was over the excess of oxygen was removed by melted phosphorus, after the method of Ramsay and Travers.

In the majority of cases, where the quantity of inert gas was considerable, the residue left after absorption by phosphorus amounted to something like 10 to 30 cubic millimetres, which was still a considerable multiple of the volume of the inert gases. It seems scarcely feasible to isolate minute quantities of these gases perfectly by the method of sparking, though I have not paid particular attention to the causes of failure. The final purification was effected in the vacuum tube in which the gas was to be spectroscopically examined. This tube was provided with electrodes of the liquid alloy of sodium and potassium, which, under the influence of the discharge, absorbs all traces of nitrogen, hydrogen, and carbon compounds. I am indebted for the knowledge of this invaluable method to Sir James Dewar. It has also been described by Mey.† After the gas in the vacuum tube had been sparked for a few minutes, the spectrum showed nothing but the inert gases. Helium was usually conspicuous at this stage. Argon, however, was rarely, if ever, completely absent from the spectrum. To isolate helium, Sir James Dewar's admirable method of absorption with

* The closed end must not be raised to more than a dull red heat, for the sake of the soldered joint.

† 'Verhand. Deutschen Phys. Gesellschaft,' vol. 5, p. 72, 1903.

cooled charcoal was employed. I have found that cooling to -80° , with carbonic acid snow in alcohol, suffices for the purpose when the quantity of gas to be absorbed is small. This is a great convenience in a laboratory which is not provided with the means of producing liquid air.

Connection was opened between the vacuum tube and a small vessel containing cocoanut charcoal at -80° C., which had been freed from occluded gases by preliminary heating and exhaustion. In a few minutes the spectrum of argon became practically invisible. In most cases a brilliant helium spectrum remained.* In order to measure the volume of the inert gases, either before or after the charcoal separation, a modified McLeod gauge was used, so arranged that the gas could be drawn into it from the rest of the apparatus, or replaced. The bulb of the McLeod gauge had a volume very large compared with the vacuum tube and charcoal reservoir. Thus nearly all the gas could be drawn into it when the mercury was lowered. The construction and method of manipulation will be apparent from fig. 2, with the explanation appended.

Until we know how much of the known radio-active bodies are present in a mineral, it is obviously impossible to say how far the helium in it may be derived from any other source. For this reason it formed an essential part of the present investigation to determine the quantity of radium in each of the minerals examined. The nearly universal presence of this element in rock-forming minerals† justified a suspicion that it would also be found in metalliferous ores, as well as in other siliceous minerals. This anticipation has been confirmed. The methods used for determining radium were those described in a former paper.‡

§ 3. *Statement of Experimental Results.*

This first set of results refers to minerals which are quite strongly radio-active and (for the most part) quite rich in helium. These results are taken from a former paper§ and are given here for convenience only. They seem to establish a kind of scale which shows roughly what ratio is to be expected between helium in a mineral and the uranium it contains. Many radio-active minerals contain considerable quantities of thorium, and in these cases the ratio is higher than usual. In this list only those minerals in which the uranium series contributes the greater part of the activity

* When the quantity of argon was appreciable, as in igneous rocks, the charcoal treatment had to be repeated more than once.

† 'Roy. Soc. Proc.,' A, vol. 78, p. 152.

‡ 'Roy. Soc. Proc.,' A, vol. 77, p. 474.

§ 'Roy. Soc. Proc.,' March 2, 1905.

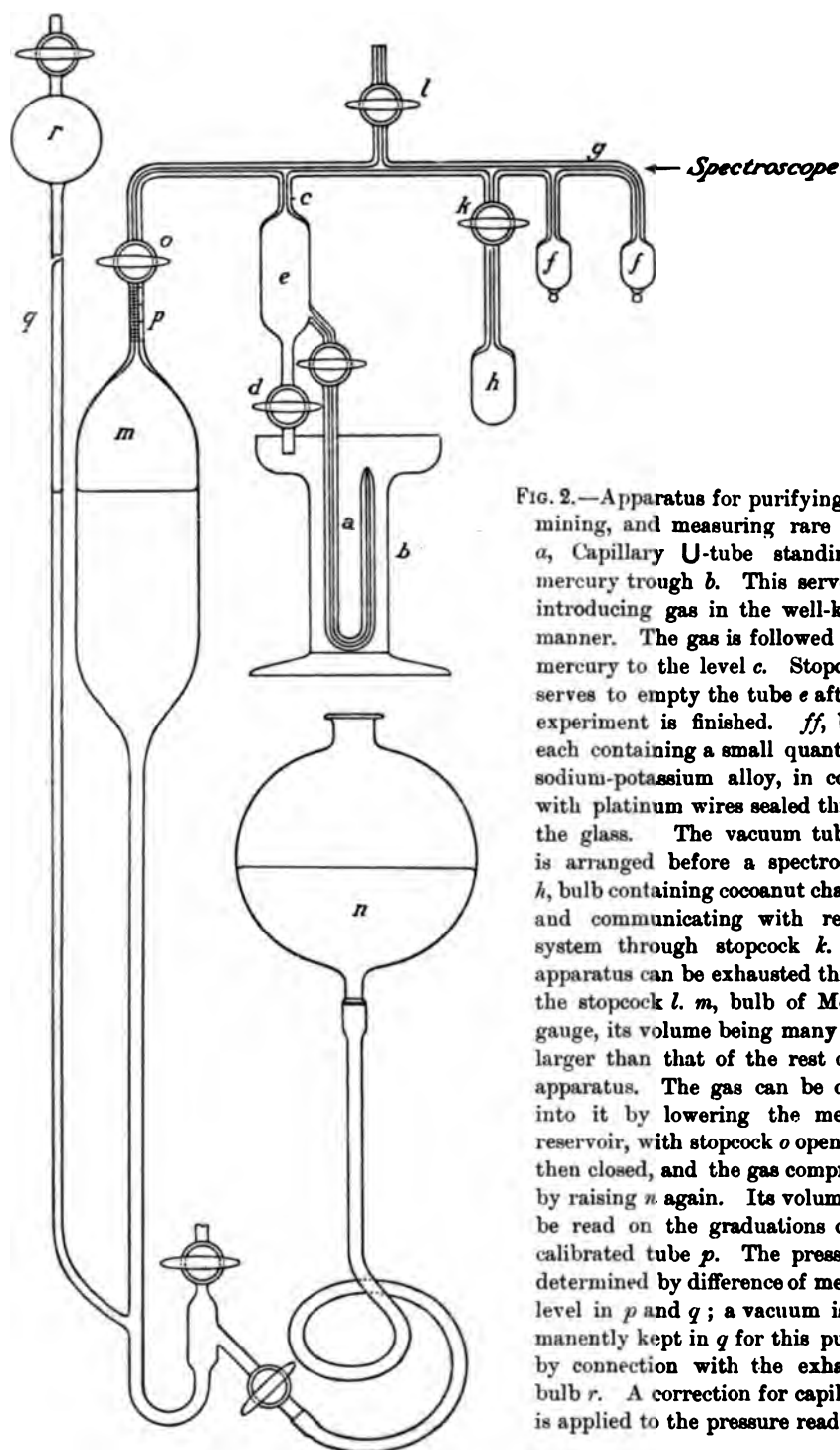


FIG. 2.—Apparatus for purifying, examining, and measuring rare gases. *a*, Capillary U-tube standing in mercury trough *b*. This serves for introducing gas in the well-known manner. The gas is followed up by mercury to the level *c*. Stopcock *d* serves to empty the tube *e* after an experiment is finished. *ff*, bulbs, each containing a small quantity of sodium-potassium alloy, in contact with platinum wires sealed through the glass. The vacuum tube *fgf* is arranged before a spectroscope. *h*, bulb containing cocoanut charcoal, and communicating with rest of system through stopcock *k*. The apparatus can be exhausted through the stopcock *l*. *m*, bulb of McLeod gauge, its volume being many times larger than that of the rest of the apparatus. The gas can be drawn into it by lowering the mercury reservoir, with stopcock *o* open. *o* is then closed, and the gas compressed by raising *n* again. Its volume can be read on the graduations of the calibrated tube *p*. The pressure is determined by difference of mercury level in *p* and *q*; a vacuum is permanently kept in *q* for this purpose by connection with the exhausted bulb *r*. A correction for capillarity is applied to the pressure readings.

are given. I have also excluded substances like torbernite and carnotite, which are obviously of secondary and quite recent origin.

Table I.

| Mineral. | Locality. | Helium, c.c. per gramme. | Grammes uranium oxide (U_3O_8) per 100 grammes. | c.c. helium per gramme uranium oxide. |
|-------------------|----------------------------------|-----------------------------|--|--|
| Pitchblende | Joachimsthal..... | 0·107 | 73·5 | 0·146 |
| Pitchblende | St. Stephen's Mine, Cornwall... | 0·10 | 21·23 | 0·472 |
| Æschynite | Hitteroe, Norway..... | 1·09 | 9·42 | 11·6 |
| Samaraskite | N. Carolina | 1·5 | 10·3 | 14·5 |
| Cyrtolite | Llano, co. Texas | 1·15 | 3·67 | 31·4 |
| Sipilite | Little Friar Mt., Virginia | 0·59 | 2·86 | 20·7 |
| Euxenite | Arendal, Norway | 0·73 | 2·84 | 25·7 |
| Microilite | Amelia Court House, Virginia | 0·05 | 1·89 | 2·64 |

The results quoted show that 10 is a normal value for the helium ratio, though values as high as 30 occur. The low value for pitchblende has long seemed anomalous, and will not appear less so in comparison with the results of the present paper, showing normal values for most of the other Cornish vein-minerals.

Table II gives a list of results for minerals containing the rare earths and some other rare elements. It will be noticed that the helium content is in several cases in excess of what the uranium present can account for, and in one case (fluor from Ivitgut, Greenland) enormously in excess.* I regard this excess of helium as due to the radio-activity of thorium contained in the mineral. In all the cases marked thus † thorium was looked for and detected by its emanation. Although no strictly quantitative experiments were made, the amount of thorium emanation appeared amply sufficient to account for the helium present.

I have failed to find minerals containing the rare earths which are reasonably free from both uranium and thorium. Accordingly a good deal of helium is always present, and it is impossible to be sure that a part of it is not contributed by other constituents such as cerium. But the determinations afford no positive support for such a view, and any such contribution must be very small compared with the contribution made by an equal mass of uranium or thorium.

In none of these cases was evidence obtained of the presence of rare gases other than helium. If any argon or neon was present, its quantity must have been quite insignificant in comparison. The inert residue always gave the brilliant yellow glow of pure helium.

* See 'Roy. Soc. Proc., A, vol. 80, p. 56.

Table II.—Rare Earth Minerals. Less Active Class.

| Mineral, with list of principal constituents. | Locality. | Quantity taken, grammes. | Helium extracted by heat, c. mm. | Helium extracted by heat, c. mm. per 100 grammes. | Grammes radium per 100 grammes. | Grammes uranium oxide per 100 grammes, calculated. | Helium ratio. |
|---|-----------------------|--------------------------|----------------------------------|---|---------------------------------|--|---------------|
| Zircon, Zr.Si.O | Kimberley..... | 55 | 6.77 | 12.3 | 1.91×10^{-9} | 5.9×10^{-3} | 4.4 |
| Eudialite, Zr.Ca.FeSiO | Greenland..... | 74 | 108 | 146 | 1.26×10^{-9} | 3.9×10^{-3} | 81.0† |
| Orthite, Ce.La.Yt.Al.FeSi.O | Sweden | 25 | 55 | 220 | 2.86×10^{-8} | 7.3×10^{-3} | 6.6 |
| Gadolinite, Yt.Ce.Fe.SiO | Hitteroe, Norway .. | 36 | 380 | 1060 | 1.86×10^{-8} | 4.2×10^{-3} | 50.0† |
| Keilhauite, Yt.Ti.Ca.Al.FeSi.O .. | Alve, Norway | 16 | 260 | 1630 | 4.53×10^{-8} | 1.4×10^{-1} | 23.0 |
| Niobite, Nb.Ta.Fe.O | Haddam, Connecticut | 125 | 450 | 360 | 9.7×10^{-9} | 3.0×10^{-3} | 5.7 |
| Apatite, Ca.P.O.F., with traces of Ce, etc. | Canada | 240 | 280 | 116 | 1.46×10^{-9} | 4.5×10^{-3} | 53.0† |
| Fluor, with rare elements..... | Ivigut, Greenland ... | 1000 | 27,000* | 2700 | 1.58×10^{-10} | 4.9×10^{-4} | 5600† |
| Cerite, Ce.La.Dy.Si.H.O | Bastnaes, Sweden ... | 65 | 82 | 126 | 3.0×10^{-9} | 9.3×10^{-3} | 27 |

* Determination by Professor Julius Thomsen.

Tables III, IV, V include a selection of minerals of varied composition, for the most part containing only traces of uranium. The helium is never distinctly in excess of what uranium and its products will account for. It should be explained that a good many of the experiments were made before any adequate apparatus had been set up for quantitative measurement. Helium, qualitatively observed, is entered as He. In such cases the quantity was not at most in excess of 2 cubic millimetres, judging by the appearance of the discharge. Usually it was very much less.

With regard to argon, the spectrum was generally seen, but the quantity was never more than 2 cubic millimetres, and never in excess of probable contamination from air.

Where the quantity of helium was insignificant, the argon spectrum was comparable with it in intensity. In such cases a query is entered under argon, to show that it may possibly occur in quantity comparable with helium. Where helium was more abundant, the argon spectrum was always inconspicuous. To distinguish these cases argon is entered as 0. But it must be repeated that there is no evidence of its presence in either of these cases.

It would seem probable that the minerals in these tables are very free from thorium. They occur for the most part in mineral veins and ore deposits, being contrasted in this respect with many of those in Tables I and II, which are primary constituents of igneous rocks.

Thorium was specially looked for in wolfram, but was not found.

The next set of experiments refers to igneous rocks. It will be observed that the helium ratio is of the same order as usual. The Irish basalt was erupted in tertiary times, and solidified long after the formation of the majority of minerals examined. However, as pointed out in a previous paper, a part of the helium now present was in all probability dissolved or entangled in the original magma. It is worthy of remark that the Cornish granite shows a considerably smaller ratio than some of the minerals of the veins which traverse it, and which are clearly younger. This may, perhaps, be partly due to the fact that a great part of the radio-active material in this granite is contained in the mica, which from its structure may be unable to retain helium. However, in view of the imperfect extraction of helium from some minerals by heat, anomalies of this kind must be expected in any case. As already mentioned, it is hoped to study the subject in this aspect later.

The quantities of argon found in these rocks are considerably smaller than those given formerly.* This is to be explained by the imperfection of the experimental method then adopted. It was assumed that after sparking

* 'Roy. Soc. Proc.,' A, vol. 79, p. 436.

Table III.—Sulphides, Selenides, and Arsenides.

| Mineral, with list of principal constituents. | Locality. | Quantity taken, grammes. | Helium extracted by heat, c. mm. | Argon extracted by heat, c. mm. | Grammes radium per 100 grammes. | Grammes uranium oxide per 100 grammes, calculated. | c.c. helium per gramme uranium oxide. |
|---|--------------------------------|--------------------------|----------------------------------|---------------------------------|---------------------------------|--|---------------------------------------|
| Galena, Pb.S | Nenthead, Cumberland | 1187 | 0.9 | ? | 2.91×10^{-12} | 9.0×10^{-6} | 17 |
| Smaltite, Co.As | ... | 277 | He | ? | 1.46×10^{-10} | 4.5×10^{-4} | — |
| Cinnabar, Hg.S | Almaden, Spain | 100 | 0 | 0 | — | — | — |
| Bornite, Cu.Fe.S | Cornwall | 259 | 30.5 | 0 | 1.04×10^{-9} | 3.2×10^{-3} | 7.4 |
| Stibnite, Sb.S | New South Wales | 225 | 1.6 | ? | 4.20×10^{-11} | 1.3×10^{-4} | 7.8 |
| Clausthalite, Pb.Se | Cachenta, Mexico | 36 | He | ? | — | — | — |
| Molybdenite, Mo.S | Renfrew, co. Ontario, Canada | 96 | He | ? | — | Rs | — |
| Blende, Zn.S | Minerva Mine, Wrexham, Denbigh | 560 | 0.37 | ? | 2.27×10^{-11} | 7×10^{-5} | 2.0 |
| Blende, Zn.S (In) | Freiberg | 40 | He | ? | — | — | — |
| Blende, Zn.S (Ga) | Bensberg | 150 | He | ? | — | — | — |
| Lorandite, Tl.As.S | ... | 1.5 | He | ? | — | — | — |
| Tin pyrites, Sn.Cu.Zn.Fe.S | Cornwall | 317 | 1.45 | ? | 1.00×10^{-11} | 3.1×10^{-5} | 29 |
| Argyrodite, Ag.Ge.S | Freiberg | 0.7 | He | ? | — | — | — |
| Cadmium Blende, Cd.S | Prisbran, Bohemia | 10 | He | ? | — | — | — |

TABLE I. New Minerals and Ores

| Mineral or Ore | Locality | Formula | Crystallographic Data | Physical Properties | Chemical Analysis |
|--|------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| Silver, Ag | Rocky Mt., Colorado | Ag | Ag | Ag | Ag |
| Copper, Cu | Monrovia, Virginia | Cu | Cu | Cu | Cu |
| Iron, Fe | Great Bear Island, Greenland | Fe | Fe | Fe | Fe |
| Bismuth, Bi | Australia | Bi | Bi | Bi | Bi |
| Tellurium, Te | Passaic, Pennsylvania | Te | Te | Te | Te |
| Graphite, C | Barro Colorado, Costa Rica | C | C | C | C |
| Hematite, FeO | Canada | FeO | FeO | FeO | FeO |
| Cassiterite, SnO ₂ | St. Austell, Cornwall | SnO ₂ | SnO ₂ | SnO ₂ | SnO ₂ |
| Chromite, Cr ₂ FeO ₄ | Udall, Maryland | Cr ₂ FeO ₄ | Cr ₂ FeO ₄ | Cr ₂ FeO ₄ | Cr ₂ FeO ₄ |
| Ilmenite, TiFeO | Ilmenok, Norway | TiFeO | TiFeO | TiFeO | TiFeO |
| Cuprite, Cu ₂ O | Wharf, Portland, Cornwall | Cu ₂ O | Cu ₂ O | Cu ₂ O | Cu ₂ O |
| Corundum, Al ₂ O ₃ | Ilmenok, Norway | Al ₂ O ₃ | Al ₂ O ₃ | Al ₂ O ₃ | Al ₂ O ₃ |

Table V.—Miscellaneous.

| Mineral, with list of principal constituents. | Locality. | Quantity taken, grammes. | Helium extracted by heat, c. mm. | Argon extracted by heat, c. mm. | Grammes radium per 100 grammes. | Grammes uranium oxide per 100 grammes, calculated. | c.c. helium per gramme uranium oxide. |
|---|------------------------------------|--------------------------|----------------------------------|---------------------------------|---------------------------------|--|---------------------------------------|
| Wolfram, W.Fe.O | East Pod Mine, Illogan, Cornwall | 207 | 240 | 0 | 3.89×10^{-9} | 1.06×10^{-2} | 22 |
| Scheelite, W.Ca.O | Cornwall | 40 | He | ? | — | — | — |
| Vanadinite, V.Pb.O | Dumfries | 300 | 0 | ? | — | — | — |
| Triphylene, Li.Mn.P.O... | Grafton, New Hampshire | 310 | He | ? | — | — | — |
| Barytes, Ba.S.O | Pallafiat, St. Bees, Cumberland... | 500 | 0.43 | ? | 1.42×10^{-10} | 4.4×10^{-4} | 0.38 |
| Celestine, Sr.S.O | Zate, Gloucestershire | 1825 | 0.75 | ? | 8.39×10^{-11} | 2.6×10^{-4} | 0.27 |
| Fluor spar, Ca.F. | Wheal Mary Anne, Cornwall ... | 250 | He | ? | — | — | — |
| Calcite, Ca.C.O | Cumberland | 1289 | <0.74 | ? | 7.10×10^{-12} | 2.2×10^{-6} | <5.4 |
| Embolite, Ag.Br.Cl | Broken Hill, New South Wales... | 20 | He | ? | — | — | — |
| Iodyrite, Ag.I | Broken Hill, New South Wales... | 30 | He | ? | — | — | — |

Table VI.—Igneous Rocks.

| Rock. | Locality. | Quantity taken, grammes. | Helium extracted by heat, c. mm. | Argon extracted by heat, c. mm. | Grammes radium per 100 grammes. | Grammes uranium oxide per 100 grammes, calculated. | c.c. helium per gramme uranium oxide. |
|-----------------|--------------------------------------|--------------------------------|---|--|---------------------------------------|--|--|
| Granite | Cornwall | 660 | 19.0 | 7.5 | 2.81×10^{-10} | 8.7×10^{-4} | 6.66 |
| Diorite | Mt. Sorrel, Leicestershire | 1200 | 6.24 | 20.3 | 6.45×10^{-11} | 2.0×10^{-4} | 5.2 |
| Phonolite | Trafalgar Law, Haddingtonshire | 820 | 7.1 | 10.8 | — | — | — |
| Basalt | Ireland | 1190 | 2.25 | 3.0 | 6.13×10^{-11} | 1.9×10^{-4} | 2.0 |

and removal of oxygen the residue might be measured as argon + helium. Further experiment has shown that the volume measured after the spectroscopic purification in the vacuum tube itself is much smaller. This, of course, only applies to very small volumes of gas. Large volumes can readily be purified by sparking.

Table VII gives results for siliceous minerals other than igneous rocks. In no case is the quantity of helium considerable, and in no case is there reason to regard it as proceeding from any other source than the uranium series. In view of the small quantity of uranium and radium in quartz, this mineral affords a severe test case for the possible production of helium from common elements.

It will be noted that flint from the upper chalk, which is geologically recent compared with most of the materials examined, shows, in accordance with anticipation, a very much lower helium ratio.

In the several samples of quartz examined, there seems to be evidence of the presence of argon in excess of what can be explained by atmospheric contamination, though the margin is not large. In garnierite, the presence of argon seems certain. The determination quoted is only one of several, all of which were believed to be unexceptionable, and all of which pointed to about the same quantity. I am inclined to suspect that the presence of traces of argon in siliceous material is general, though certainty could only be achieved with great labour. Something more will be said on this subject in a later paragraph.

The first four sets of determinations in Table VII, which are only samples of many similar ones, refer to the mineral beryl. This mineral has proved altogether exceptional. It will be observed that the helium present is, as a rule, enormously in excess of what can be attributed to uranium and its series. This raises the question of whether thorium is present. For this, as for further investigations on the subject, I used the beryl richest in helium, that found at Acworth, New Hampshire.*

Thorium emanation could, indeed, be just detected by careful experiments in a considerable quantity (50 grammes) of Acworth beryl in solution. But the thorium series does not appear to contribute more, if so much, to the total radio-activity of the mineral as does the uranium series, and affords no explanation of the quantity of helium present.

With the idea that some unknown radio-active constituent might be present which did not yield an emanation, the powdered beryl was carefully tested with an electroscope for radio-activity. Nothing could be detected,

* Another sample of beryl from the same place, somewhat more transparent than the foregoing, contained much less helium.

Table VII.—Silica and Silicates.

| Mineral, with list of principal constituents. | Locality. | Quantity taken, grammes. | Helium extracted by heat, c. mm. | Helium extracted by heat, c. mm. per 100 grammes. | Argon extracted by heat, c. mm. | Grammes radium per 100 grammes. | Grammes uranium oxide per 100 grammes. | c.c. helium per gramme uranium oxide. |
|---|---------------------------------------|--------------------------|----------------------------------|---|---------------------------------|---------------------------------|--|---------------------------------------|
| Quartz, Si.O | Madagascar | 1250 | 2.4 | 0.192 | 3.16 | 1.39×10^{-11} | 4.29×10^{-4} | 9.0 |
| Quartz, Si.O | From veins in slate, Ilfracombe | 1187 | 1.43 | 0.121 | 2.5 | 7.45×10^{-12} | 2.31×10^{-4} | 10.4 |
| Quartz, Si.O | Brazil | 1015 | 0.74 | 0.073 | 2.0 | — | — | — |
| Quartz sand, Si.O .. | | 300 | 0.55 | 0.183 | ? | 1.94×10^{-11} | 6.0×10^{-4} | 6.0 |
| Flint, Si.O | From chalk, Brandon, Norfolk | 1275 | 0.295 | 0.023 | 1.9 | 4.30×10^{-11} | 1.33×10^{-4} | 0.246 |
| Garnierite, Ni.Si.O.H | Oregon | 920 | 2.5 | 0.272 | 6.4 | — | — | — |
| Lepidolite, LiAlSi ₃ (Rb) (Cs) O | Auburn, Maine, U.S.A. | 250 | He | — | ? | — | — | — |
| Rhodonite, Mn.Si.O | Cornwall | 182 | He | — | ? | 1.49×10^{-10} | 4.6×10^{-4} | — |
| Topaz, Al.Si.O.F .. | Brazil | 50 | He | — | ? | — | — | — |
| Orthoclase, KAlSi ₃ O | Glass Mine, Rocks, Cornwall | 250 | He | — | ? | Ra | — | — |
| Spodumene, LiAlSi ₂ O | Brazil | 10 | He | — | ? | — | — | — |
| Pallux, Cs.AlSiO .. | Hebron, Maine | 2 | 0 | — | 0 | — | — | — |
| Tourmaline, Al.B. Mg.SiO, etc. | Madagascar | 230 | He | — | ? | Ra | — | — |

though other minerals containing much less helium showed a conspicuous activity when tested in this manner, in virtue of the radio-active constituents present. The following results illustrate this.

A correction for the ordinary leak of the electroscope (0.40 div. per hour) has been applied.

| Mineral. | Helium, c.c. per 100 grammes. | Rate of electroscope leak. Scale div. per hour. |
|---------------|----------------------------------|--|
| Beryl..... | 1.68 | 0.03 ? |
| Niobite | 0.36 | 8.45 |
| Cerite..... | 0.13 | 0.86 |
| Zircon | 0.12 | 1.06 |
| Wolfram | 0.12 | 0.46 |

Thus it appears impossible to connect the helium in beryl with radio-activity in the ordinary sense of the word.

It was next attempted to see if helium in comparatively large quantities could be connected with any recognised constituent of beryl, without regard to radio-activity. Beryllium seemed the most promising constituent. Several other beryllium minerals such as phenacite and chrysoberyl, were tried, as recorded above. But only those traces of helium were found which are almost universal, and which I attribute to traces of the radio-active elements. Cæsium has been found in some beryls, but the absence of helium from the cæsium mineral, pollux (see Table VII), makes it unlikely that this element is concerned. Moreover, the cæsium lines were not visible in the flame spectrum of my beryl. The remaining important constituents of beryl are comparatively common, and are amply represented in the tables of minerals given above, so that they, too, must be excluded. Examination of the flame spectrum of Acworth beryl revealed the presence of indium, but in less quantity than in Freiberg blende; and Freiberg blende yields little helium.

The above paragraphs summarise the experimental evidence which I have been able to obtain on this question, without affording any positive answer to it. It is difficult to find any advantageous ground from which to attack it further.

A few words may be said on some possible explanations:—

(1) It may be suggested that these beryls have formerly contained radio-active elements, but that these have now decayed, their transformations being completed.

The objection to this view is that nearly all the evidence we have points to an unalterable rate of radio-active transformation. Thus the explanation

Table VIII.—Beryls and other Beryllium Minerals.

| Mineral, with list of constituents. | Locality. | Quantity taken, grammes. | Helium extracted by heat, c. mm. | Argon extracted by heat, c. mm. | Grammes radium per 100 grammes. | Grammes uranium oxide per 100 grammes. | c.c. helium per gramme uranium oxide. |
|--------------------------------------|------------------------------|--------------------------|----------------------------------|---------------------------------|---------------------------------|--|---------------------------------------|
| Beryl, Be.Al.SiO.Li ... | Acworth, New Hampshire | 250 | 4200 | 0 | 1.13×10^{-9} | 3.5×10^{-3} | 954 |
| Beryl " | Chester, Pennsylvania | 81 | 550 | 0 | 7.10×10^{-10} | 2.2×10^{-3} | 620 |
| Beryl " | Arendal, Norway | 63 | 153 | 0 | 2.39×10^{-9} | 7.4×10^{-3} | 66 |
| Beryl " | Massachusetts, U.S.A. | 16 | 5.1 | 0 | 3.23×10^{-11} | 1.0×10^{-4} | 628 |
| Phenacite, Be.SiO ... | Takavaya, Siberia | 38 | (He) | ? | — | — | — |
| Chrysoberyl, BeAlO ... | Ceylon | 52 | He | ? | — | — | — |
| Chrysoberyl " | Haddam, Connecticut | 65 | He | ? | — | — | — |
| Melliphanite, Be.Al. Ca.SiO | Brevig | 9 | He | ? | — | — | — |
| Beryllonite, Be.NaP.O | Stoneham, Maine | 9 | He | ? | — | — | — |

mentioned would require the assumption that beryls generally were much older than other minerals of the earth's crust. The circumstances of their occurrence, geologically considered, are not consistent with this assumption.

(2) It may be supposed that the helium found in beryls was not generated *in situ* at all, but was chemically absorbed or occluded by the material in the course of solidification. I cannot think this in any way probable. Other siliceous minerals do not absorb helium in this way, for they contain none that may not be otherwise accounted for. Nor does anything we know of the properties of helium suggest that it is likely to have a violent preference for beryl.

(3) There may be an unknown element present in beryl which has escaped detection, for want of well marked chemical peculiarities; and this unknown element may emit α -particles with less than the critical velocity, as suggested in the introduction (p. 572). On this double hypothesis the facts would be explained. But naturally an explanation so speculative has in itself little scientific value.

§ 4.—*Helium and Radio-activity of Ordinary Elements.*

The results above recorded are not in favour of the theory that the common elements are perceptibly radio-active. This seems clear from the following considerations. It is known that radium, actinium, and thorium* give rise to helium. There is no evidence which to me, at least, appears convincing that any one of the undoubtedly radio-active bodies does not give rise to it. Accordingly, we may provisionally regard the formation of helium as a criterion of radio-activity.

It is well known that there is an ionising radiation from the walls of any vessel which ionises the contained air. The question to be faced is whether any important part of this radiation is of the same nature as the α -rays of radium.

In determining the radium content of galena (see Table III), 200 grammes of the mineral were stored in solution, so as to allow the emanation to accumulate. The emanation was boiled out and introduced into an electroscope and allowed to form the active deposit. After this the leak of the electroscope was increased by about one-quarter of its normal amount. Now this increased leak is of the same order as the total ionising power of the uranium series of bodies present in 200 grammes of the mineral, when exercised freely, without enfeeblement, owing to unproductive absorption of the rays by solids. The electroscope case was a glass bulb 10 cm. in diameter, or about 314 sq. cm. in area. As the α -rays are not able to penetrate from a depth of more than

* 'Roy. Soc. Proc.,' A, vol. 80, p. 56.

about 0.004 cm., it follows that the total quantity of glass which can come into action in ionising the enclosed air cannot be much more than 314×0.004 c.c., or about 3.5 grammes. The ionisation produced by this quantity of glass is greater than that produced by the radio-active impurities in 200 grammes of galena. The normal ionisation in vessels of other common materials is not very different. It may be concluded that in a mineral like this galena the apparent activity contributed by the common elements (lead and sulphur) is at least a hundred times that due to the radio-active impurities. As these impurities are present in sufficient quantity to account for the helium found, it follows that enormously larger quantities of helium would be expected if the ionising properties of the common elements were really of radio-active origin.

The lists of results which have been given afford many other cases of minerals free enough from radium to emphasise the same conclusion. There is no indication that the helium ratio increases as the radio-active impurities diminish in amount.*

It is evidently of great interest to push the enquiry into possible helium production by common elements as far as possible; for although their radio-activity seems to be much smaller than might be expected from the ionising power, it is not, for that reason, necessarily non-existent.

I have found that gypsum, rock salt, and the various saline minerals of Stassfurt are for the most part much less contaminated with radium than minerals of any other class. In most cases helium can scarcely be detected in them; but in one or two instances results have been obtained which call for further investigation. It is hoped to complete these experiments shortly.

§ 5. *Presence of Argon and Neon in Minerals.*

The interest of this subject has already been referred to. It has been recorded that siliceous materials in general appear to contain a little argon, and that igneous rocks certainly always do so. The question now arises of whether the argon is due to radio-active changes, as might appear not improbable from Sir William Ramsay and Mr. Cameron's results.

It might perhaps be supposed that the conditions of radio-active change were so modified in these materials as to result in the partial substitution of argon for helium. Upon the whole I do not regard this supposition

* It seems likely from the results of MacLennan ('Phil. Mag.,' [6], vol. 14, p. 760, 1907) and Elster and Geitel, that other samples of galena will be found much less free from radio-active impurities than that which I examined. For their results point to great variety in the quantities of polonium in various samples of commercial sheet lead.

favourably. In siliceous minerals like zircon, which are fairly active, the argon content is infinitesimal in comparison with the helium content. This appears from the experiments already quoted. Some other experiments, specially directed to this point, which were made before the systematic investigations here recorded, bring it out more clearly: 12.8 c.c. of helium was extracted by heating a large quantity of zircon. The argon contained in this was separated by charcoal cooled in liquid air, and was certainly less than 0.03 c.c. Again, 37.6 c.c. of helium from cyrtolite, another radio-active silicate, contained at most 0.02 c.c. argon. In these cases, therefore, the argon does not greatly exceed a thousandth part of the helium and may be much less, for the experiments were made before very much experience had been gained, and considerable atmospheric contamination is not improbable. The quantity of argon in active silicates is not large,* and it may be concluded that it is not connected with their activity. Similar experiments made with large quantities of helium from monazite, samarskite, and thorianite proved that the argon in these cases did not at most exceed a thousandth part of the helium.

The small quantities of argon in question may, I think, be very well regarded as derived from the atmosphere during the formation of the various minerals.

With regard to neon, the available data are very scanty. Its presence was, as a rule, masked by helium which, when present in excess, altogether extinguishes the yellow neon line. The difficulty can be overcome by separation with charcoal in liquid air. This has not usually been available to me, and carbonic acid cooling does not suffice for the absorption of neon. In a few cases of igneous rocks, neon has been observed as recorded in a former paper.† I separated spectroscopic traces of neon from the small quantity of argon from zircon and cyrtolite mentioned above. A letter to 'Nature' was published to this effect, but in the light of subsequent experience no importance can be attached to the observation. A very small quantity of air suffices to bring in the neon spectrum quite distinctly:

* It is necessary to refer to a very perplexing case. The mineral malacone, which is a hydrous silicate of zirconium of considerable activity, was found by Ramsay and Travers ('Roy. Soc. Proc.' vol. 60, 1897, p. 444), and subsequently by Kitchin and Winterson ('Chem. Soc. Trans.' vol. 89, 1906, p. 1570) to contain much argon along with helium. I have failed altogether to confirm this result. Several specimens of the mineral (which came from Hitteroe, Norway) were examined, they gave nothing but a brilliant yellow helium glow, argon being practically invisible. I cannot doubt the genuineness of the specimens, for they correspond closely to those from the same locality in the Natural History Museum, South Kensington.

† 'Roy. Soc. Proc.' A, vol. 79, p. 437.

594 *Helium and Radio-activity in Rare and Common Minerals.*

1 c.c. is ample, and with care 1/10 c.c. is enough. In some other cases I have suspected neon, but can make no positive statement.

§ 6. *Summary of Conclusions.*

1. Helium can be detected in almost all the minerals of the earth's crust.
2. The quantity is in most cases about what might be anticipated from the traces of uranium and radium which the minerals contain. This is illustrated by the following selected results, which are given in round numbers only.

| Mineral. | Helium present, c. mm. per kilo. | Helium ratio, <i>i.e.</i> , ratio of helium to uranium oxide. |
|-------------------|-------------------------------------|---|
| Samaraskite | 1,500,000 | 14 |
| Hæmatite | 700 | 9 |
| Galena..... | 2 | 17 |
| Quartz..... | 2 | 10 |

3. Where much higher helium ratios than the above have been observed, the excess of helium can always be connected with the presence of thorium, except in one outstanding case. Thus the experiments afford no evidence in favour of helium production by radio-activity of ordinary elements.

4. The outstanding case is beryl, which contains abundance of helium, without anything approaching a sufficient radio-activity to explain its presence. This helium cannot be connected with any known constituent of beryl.

5. Igneous rocks, and probably siliceous minerals generally, contain small quantities of argon. In other minerals its quantity is negligible, at all events in comparison with the helium present. Nor is there any indication that it increases with the amount of radio-active material.

Effect of a Cross Wind on Rifled Projectiles.

By A. MALLOCK, F.R.S.

(Received May 5,—Read May 28, 1908.)

The effect of wind on rifled projectiles is important for practical reasons, especially in the case of small arms, but the object of the present note is not so much to determine the actual effect of wind as to show that accurate experiments on the subject would afford valuable information concerning the flight of projectiles in still air.

It is easily shown that if the air resistance acts always in the direction of the resultant of the velocities of the wind and the projectile, the angle made by the resultant velocity with the line of aim remains constant throughout the range and is independent of the law connecting velocity and retardation.*

In order, however, that the resistance may act in the direction of the resultant velocity, the projectile must be symmetrical about that direction. This, in the case of any form except a sphere, means that the principal axis of the projectile must take the direction of the resultant velocity.

If this is assumed and we take v_0 as the initial velocity of the shot, w as the velocity of the wind (w/v_0 being small) and ξ and η as the co-ordinates of the shot parallel and perpendicular respectively to the line of aim, ξ being measured from a moving origin at $v_0 t$; we have at the time t

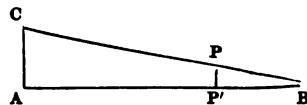
$$v = v_0 - \xi, \quad R = v_0 t - \xi, \quad \text{and} \quad \eta = \xi w / v_0;$$

hence
$$\eta = \frac{w}{v_0} (v_0 t - R) \quad \text{or} \quad w \left(t - \frac{R}{v_0} \right). \quad (1)$$

This result was first given by Captain Younghusband, R.N., and would be correct if the axis of the projectile set itself in the direction of the resultant velocity from the very beginning.

At first, however, the axis makes an angle w/v_0 with the velocity resultant, and the resistance has therefore a horizontal component at right angles to

* Let AB be the initial velocity and direction of the shot. AC the velocity and direction of the wind. The resultant velocity of the shot through the air is CB. Let



CP be the velocity after the air resistance has given the shot a negative velocity BP in the direction BC. The components of the resultant velocity parallel and perpendicular to AB are $AB - PB$ and $AC - PP'$, and their ratio AC/AB as before.

that resultant, for the same reason that a small angle between the axis of the projectile and the tangent to the trajectory produces an upward force on the former.

The difference between the two cases lies in the fact that whereas the angle between the axis and the tangent (and therefore also the upward force) must remain finite throughout the range, the horizontal lateral force diminishes indefinitely with the time and, for the greater part of a long range, the direction of the axis of the projectile and the velocity resultant may be taken as identical. The reason for this is, of course, the constancy of the direction of the velocity resultant.

The question then as to how far (1) may be looked on as giving a true value for the effect of the wind turns on the rate at which the projectile can set its axis in the direction of the velocity resultant.

The couple required to turn the axis of a rifled projectile at a given angular velocity can readily be determined in terms of its mass, form, and spin, but what the angle between the axis of the projectile and the direction of its motion must be in order that the air may cause this couple to act, is not known, and cannot at present be calculated.

It is shown, however, in a former paper,* that to produce a given angular velocity of the axis of a projectile the couple must vary as the fourth power of the linear dimension.

For a given inclination of the axis to the direction of motion the couple applied by action of the air will vary as the cube of the linear dimension; thus the angular velocity of the axis will be inversely as the linear dimension; or in other words the time for a given angle will be as the linear dimensions.

For a given inclination the lateral force will be as the square of the linear dimension and the distance to which the lateral force will carry the projectile while turning through the angle w/v_0 will be proportional to the linear dimension.

Thus, instead of the expression in (1) we should write

$$\eta = AL + w(t - R/v_0), \quad (2)$$

where L denotes the linear dimension, and A some constant depending on the form, weight, and initial velocity of the projectile.

If careful experiments were made on wind deflection, the velocity of the wind being recorded at several positions along the range at the instant that each shot was fired,† the value of A might be determined, and therefrom the

* "The Behaviour of Rifled Projectiles in Air," 'Roy. Soc. Proc.' vol. 79, p. 547.

† I cannot find that any experiments of the kind have been made up to the present.

angle which the axis of a projectile fired in still air makes with the tangent to the trajectory.

Attempts have been made to measure this angle photographically, but hitherto without success, and the method here indicated, though indirect, would, I think, be more likely to attain the desired result.

On the Decay of the Radium Emanation when dissolved in Water.

By RICHARD B. MOORE, B.Sc.

(Communicated by Sir William Ramsay, F.R.S. Received May 20,—Read June 4, 1908.)

The results obtained by Ramsay and Cameron* on dissolving radium emanation in water and in copper sulphate solution have made it advisable to investigate the behaviour of the emanation, when dissolved in such solvents, from a radio-active standpoint. There are two possible explanations for the results obtained by these authors:—

(1) The one advanced by them to the effect that the α -particle is not identical with the helium atom, but that the "degradation" of the large molecule of the emanation is effected by bombardment with α -particles, the products of the degradation varying according to whether, on the one hand, the emanation is alone or mixed with other gases, or, on the other, whether it is dissolved in water or copper sulphate solution.

(2) The α -particle is a helium atom under ordinary conditions, but when the emanation is dissolved in water or copper sulphate solution an α -particle of greater mass is split off from the emanation atom.

If the latter explanation be correct the disintegration products of the emanation when it is dissolved in water or copper sulphate solution ought to be different from those obtained from the emanation when alone or mixed with air. An investigation of these disintegration products should throw light on the subject.

The present note deals with the rate of decay of the radium emanation when dissolved in water. The emanation accumulated by 110 milligrammes of radium bromide in two days, with the accompanying oxygen and hydrogen, was collected in a gas burette over mercury. After exploding, a small amount of water was run into the burette, and the solution of the emanation

* 'Chem. Soc. Trans.,' vol. 91, p. 1593, 1907.

598 *Decay of the Radium Emanation when dissolved in Water.*

thus obtained, together with the slight excess of hydrogen, was transferred to a glass tube 2 inches long and 5 mm. in diameter, which had previously been exhausted. The solution filled about five-sixths the volume of the tube. The latter was sealed, and the decay curve of the emanation was obtained by means of the γ -rays, sheet lead being used to cut down the rays to the required amount. The half-time period found was 3.8 days. It may, therefore, be assumed that the emanation decays at the same rate when dissolved in water as it does in air. The initial portion of the curve was also the same, reaching a maximum in about four hours. As the volume of the emanation used was less than 0.130 cubic millimetre and the solubility coefficient at 18°, as obtained by Kofler,* is 0.270, the ratio of the volume of the emanation in the gas phase to that in the water phase would be small.

The result obtained does not point definitely to either of the two possible theories which have been mentioned. The degradation of a portion of the emanation molecules into neon or argon atoms instead of helium atoms, would not necessarily change the time rate of decay; on the other hand, the percentage of the emanation atoms which changed per second might be the same although the mass of the α -particle varied. The real experimental test of the two theories lies in a comparison of the mass of the α -particles from the emanation when the latter is mixed with air, and when it is in solution. Some work is in progress to test this point.

* 'Phys. Zeit.,' vol. 9, pp. 6—8, 1907.

Percentage of the inactive Gases in the Atmosphere: a Correction to Previous Calculations.

By Sir WILLIAM RAMSAY, F.R.S.

(Received May 4,—Read May 7, 1908.)

Krypton and *Xenon* ('Proceedings,' vol. 71, 1903, p. 426).—The total weights calculated from the volumes are ten times too small; *instead of*

Kr = 0·0028 per cent., *read*, 0·028 per cent.

Xe = 0·0005 „ „ 0·005 „

Helium and *Neon* ('Proceedings,' A, vol. 76, 1905, pp. 113, 114).—All percentages are a hundred times too small; *instead of*

Helium by weight in gaseous air = 0·00000056 per cent., and

read „ volume „ = 0·0000040 „

Helium by weight in gaseous air = 0·000056 per cent., and

„ volume „ = 0·00040 „ ;

and *instead of*

Neon by weight in gaseous air = 0·00000086 „ and

„ volume „ = 0·0000123 „

read

Neon by weight in gaseous air = 0·00086 „ and

„ volume „ = 0·00123 „ .



INDEX to VOL. LXXX. (A)

- Abney (Sir W. de W.) The Action of Ozone on Water-colour Pigments, 146.
 Address of the President, Lord Rayleigh, November 30, 1907, 239.
 Air, determination of coefficient of viscosity of (Grindley and Gibson), 114.
 Alloys, interaction of mercury with certain (Mallet), 83.
 Alternate current measurement (Sumpner), 310.
 Ammonium nitrate, polymorphic changes of (Behn), 444.
 Ampere-standard balance (B.O.T.) compared with Ayrton-Jones current-weigher (Mather and Smith), 383.
 Anderson (T.) Report on the Eruptions of the Soufrière in St. Vincent in 1902, and on a Visit to Montagne Pelée in Martinique. Part II.—The Changes in the Districts and the Subsequent History of the Volcanoes, 281.
 Argon and helium, refractive index and dispersion (Burton), 390.
 Aston (F. W.) Experiments on a New Cathode Dark Space in Helium and Hydrogen, 45.
 Atmosphere, percentage of inactive gases in (Ramsay), 599.
 Atmospheric electric potential gradient and earth-air current, measurement of (Wilson), 537.
 Ayrton (Hertha) On the Non-periodic or Residual Motion of Water moving in Stationary Waves, 252.
 Ayrton (W. E.), Mather (T.), and Smith (F. E.) A New Current Weigher, and a Determination of the Electromotive Force of the Normal Weston Cadmium Cell, 12.

 Bakerian Lecture, 1907 (Thorpe), 298.
 Ballistics, exterior (No. 2) (Forbes), 140.
 Balloons, ascent of meteorological, and temperature of upper air (Mallock), 530.
 Behn (U.) On the Polymorphic Changes of Ammonium Nitrate, 444.
 Benzene and homologues, absorption spectra of vapour and solution at different temperatures and pressures (Hartley), 162.
 Berthelot (P. E. M.) Obituary notice of, iii.
 Beta-rays from uranium, scattering by matter (Crowther), 186; — secondary (McClelland), 501.
 Boltzmann (L.) Obituary notice of, xi.
 Brooks (E. E.) The Spectrum of Magnesium and of the so-called Magnesium Hydride, as obtained by Spark Discharges under Reduced Pressure, 218.
 Burton (W.) The Refractive Index and Dispersion of Light in Argon and Helium, 390.

 Callendar (H. L.) On Vapour Pressure and Osmotic Pressure of Strong Solutions, 466; — and Dalby (W. E.) On the Measurement of Temperatures in the Cylinder of a Gas Engine, 57.
 Cathode dark space in helium and hydrogen (Aston), 45.
 Chattaway (F. D.) A Method of Depositing Copper upon Glass from Aqueous Solutions in a thin brilliantly reflecting Film, and thus producing a Copper Mirror, 88.

- Chree (C.) Magnetic Declination at Kew Observatory, 1890—1900, 113.
- Cookson (B.) A Photographic Determination of the Elements of the Orbits of Jupiter's Satellites, 567.
- Copper, annealing of, with reference to dilatation (Turner and Levy), 1 ; — mirror, produced by depositing copper upon glass from aqueous solutions (Chattaway), 88.
- Coronal structure and prominence (Lockyer), 178.
- Crookes (Sir W.) On Scandium, 516.
- Crowther (J. A.) On the Scattering of the β -rays from Uranium by Matter, 186.
- Crystal structure and the dispersion of double refraction (Havelock), 28.
- Crystals, intimate structure of, Part VI (Sollas), 267.
- Current weigher, a new (Ayrton, Mather, and Smith), 12.
- Cuthbertson (C.) and Metcalfe (E. P.) On the Refractive Indices of Gaseous Nitric Oxide, Sulphur Dioxide, and Sulphur Trioxide, 406 ; — On the Dispersion of Gaseous Mercury, Sulphur, Phosphorus, and Helium, 411.
- Dalby (W. E.) See Callendar and Dalby.
- Darwin (Sir G. H.) Further Consideration of the Stability of the Pear-shaped Figure of a Rotating Mass of Liquid, 166.
- Dewar (Sir J.) and Jones (H. O.) Notes on the Application of Low Temperatures to some Chemical Problems: (1) Use of Charcoal in Vapour Density Determination ; (2) Rotatory Power of Organic Substances, 229.
- Diamond, conversion into coke by cathode rays (Parsons and Swinton), 184.
- Discharge of negative electricity from hot platinum, effect of hydrogen on (Wilson), 379.
- Dispersion of mercury, sulphur, phosphorus, and helium (Cuthbertson and Metcalfe), 411.
- Drysdale (C. V.) On Luminous Efficiency and the Mechanical Equivalent of Light, 19.
- Dupré (A.) Obituary notice of, xiv.
- Ear, sensibility to direction of explosive sounds (Mallock), 110.
- Earth's surface, represented by means of spherical harmonics (Love), 553.
- Electric discharge in monatomic gases (Soddy and Mackenzie), 92.
- Electrical resistance of moving matter (Trouton and Rankine), 420.
- Fawsitt (C. E.) On the Determination of Viscosity at High Temperatures, 290.
- Flow of air through a pipe, frictional resistances to (Grindley and Gibson), 114.
- Forbes (G.) Exterior Ballistics (No. 2), 140.
- Gas-engine cylinder, measurement of temperatures in (Callendar and Dalby), 57.
- Gibson (A. H.) See Grindley and Gibson.
- Gold (E.) The Relation between Wind Velocity at 1000 Metres Altitude and the Surface Pressure Distribution, 436.
- Greaves (R. H.) See Perman and Greaves.
- Grindley (J. H.) and Gibson (A. H.) On the Frictional Resistances to the Flow of Air through a Pipe, 114.
- Hartley (W. N.) The Absorption Spectra of the Vapours of Benzene and its Homologues at Different Temperatures and Pressures, and likewise of Solutions of Benzene, 162.
- Havelock (T. H.) The Dispersion of Double Refraction in Relation to Crystal Structure, 28.
- Helium and radio-activity in minerals (Strutt), 572.
- Herschel (A. S.) Obituary notice of, xix.
- Hysteresis loss in iron alloys under very small magnetic forces (Wilson and others), 548.

- Invariants, operational, of a binary quantic (MacMahon), 151.
- Ions in gases, charges on positive and negative (Townsend), 207.
- Jerusalem (G.) and Pope (W. J.) The Relation between the Crystalline Form and the Chemical Constitution of the Picryl Derivatives, 557.
- Jervis-Smith (F. J.) On the Generation of a Luminous Glow in an Exhausted Receiver moving near an Electrostatic Field, and the Action of a Magnetic Field on the Glow so produced, 212.
- Jet-vibration method of investigating surface-tension of liquids (Pedersen), 26.
- Jones (H. O.) See Dewar and Jones.
- Jupiter's satellites, photographic determination of elements of orbits of (Cookson), 567.
- Kinetic stability (Lamb), 168.
- Lamb (H.) On Kinetic Stability, 168.
- Lees (C. H.) The Effects of Temperature and Pressure on the Thermal Conductivities of Solids. Part II.—The Effect of Low Temperatures on the Thermal Conductivities of Pure Metals and Alloys, 143.
- Levy (D. M.) See Turner and Levy.
- Light, dispersion in argon and helium (Burton), 390 ; — mechanical equivalent of, and luminous efficiency (Drysdale), 19.
- Liquid, rotating, stability of pear-shaped figure of (Darwin), 166.
- Lockyer (Sir N.) On the Presence of Sulphur in some of the Hotter Stars, 50 ; — on the Observations of Sun and Stars made in some British Stone Circles. Third Note.—The Aberdeenshire Circles, 285.
- Lockyer (W. J. S.) Prominence and Coronal Structure, 178.
- Love (A. E. H.) Note on the Representation of the Earth's Surface by means of Spherical Harmonics of the First Three Degrees, 553.
- Lowry (T. M.) See Smith, Mather, and Lowry.
- Luminous glow in exhausted receiver near an electrostatic field, and action of magnetic field on (Jervis-Smith), 212.
- McClelland (J. A.) Secondary β -rays, 501.
- McClintock (Sir L.) Obituary notice of, xxiii.
- Mackenzie (T. D.) See Soddy and Mackenzie.
- MacMahon (P. A.) Preliminary Note on the Operational Invariants of a Binary Quantic, 151.
- Magnesium and magnesium hydride, spectrum of, in spark discharges (Brooks), 218.
- Magnetic declination at Kew Observatory, 1890—1900 (Chree), 113.
- Magnetism, diurnal variation of terrestrial (Schuster), 80.
- Mallet (J. W.) Results of the Interaction of Mercury with Alloys of other Metals, 83.
- Mallock (A.) Note on the Sensibility of the Ear to the Direction of Explosive Sounds, 110 ; — Note on the Trajectories of Rifled Projectiles with Various Shapes of Head, 519 ; — Note on the Ascent of Meteorological Balloons and the Temperature of the Upper Air, 530 ; — Effect of a Cross Wind on Rifled Projectiles, 595.
- Mather (T.) and Smith (F. E.) Comparison of the Board of Trade Ampere-standard Balance with the Ayrton-Jones Current-weigher ; with an Appendix on the Electromotive Forces of Standard Cells, 383. See also Ayrton, Mather, and Smith, and Smith, Mather, and Lowry.
- Medals, award of, for 1907, 246.
- Mercury, interaction with alloys of other metals (Mallet), 83.

- Metcalf (E. P.) See Cuthbertson and Metcalfe.
- Moissan (H.) Obituary notice of, xxx.
- Moore, (R. B.) On the Decay of the Radium Emanation when dissolved in Water, 597.
- Myers (C. S.) and Wilson (H. A.) On the Perception of the Direction of Sound, 260.
- Obituary notices of Fellows deceased, i; Berthelot, iii; Boltzmann, xi; Dupré, xiv; Herschel, xix; McClintock, xxiii; Moissan, xxx; Perkin, xxxviii; Russell, lx.
- O'Dell (G. F.) See Wilson, Ernest.
- Osmotic pressure of solutions (Porter), 457; (Callendar), 466.
- Ozone, decomposition by heat (Perman and Greaves), 353.
- Parsons (Hon. C. A.) and Swinton (A. A. C.) The Conversion of Diamond into Coke in High Vacuum by Cathode Rays, 184.
- Pear-shaped figure of rotating liquid (Darwin), 166.
- Pedersen (P. O.) On the Surface-tension of Liquids investigated by the Method of Jet Vibration, 26.
- Perkin (Sir W. H.) Obituary notice of, xxxviii.
- Perman (E. P.) and Greaves (R. H.) The Decomposition of Ozone by Heat, 353.
- Picryl derivatives, relation between crystalline form and chemical constitution (Jerusalem and Pope), 557.
- Polymorphic changes of ammonium nitrate (Behn), 444.
- Pope (W. J.) See Jerusalem and Pope.
- Porter (A. W.) On the Osmotic Pressure of Compressible Solutions of any Degree of Concentration. Part II.—Cases in which both Solvent and Solute are Volatile, 457.
- Projectiles, effect of cross wind on rifled (Mallock), 595.
- Quantic, operational invariants of binary (MacMahon), 151.
- Radio-activity and helium in minerals (Strutt), 572.
- Radium, atomic weight of (Thorpe), 298; — emanation, decay of, in water (Moore), 597.
- Ramsay (Sir W.) Percentage of the Inactive Gases in the Atmosphere: a Correction to Previous Calculations, 599.
- Rankine (A. O.) See Trouton and Rankine.
- Rayleigh (Lord) Presidential Address, November 30, 1907, 239.
- Refraction, dispersion of double, and crystal structure (Havelock), 28.
- Refractive index of argon and helium (Burton), 390; — of nitric oxide, sulphur dioxide and trioxide (Cuthbertson and Metcalfe), 406.
- Rotatory power of organic substances (Dewar and Jones), 235.
- Russell (H. C.) Obituary notice of, lx.
- St. Vincent and Martinique eruptions of 1902—changes in the districts and subsequent history of volcanoes (Anderson), 281.
- Scandium, on (Crookes), 516.
- Schuster, A. The Diurnal Variation of Terrestrial Magnetism, 80.
- Self-induction in an iron cylinder traversed by alternating currents, effects of (Wilson), 369.
- Smith (F. E.) On the Normal Weston Cadmium Cell, 75; — Mather (T.) and Lowry (T. M.) The Silver Voltameter, 77; — See also Ayrton, Mather, and Smith, and Mather and Smith.
- Soddy (F.) and Mackenzie (T. D.) The Electric Discharge in Monatomic Gases, 92.
- Sollas (W. J.) On the Intimate Structure of Crystals. Part VI.—Titanic Oxide, its Polymorphs and Isomorphs, 267.

- Solutions, osmotic pressure of (Porter), 457 ; (Callendar), 466.
 Sound, the perception of direction of (Myers and Wilson), 260.
 Stone circles, Aberdeenshire, observations of sun and stars made in (Lockyer), 285.
 Strutt (Hon. R. J.) Note on the Association of Helium and Thorium in Minerals, 56 ;
 — Helium and Radio-activity in Rare and Common Minerals, 572.
 Sulphur in some hotter stars (Lockyer), 50.
 Sumpner (W. E.) Alternate Current Measurement, 310.
 Surface-tension of liquids and method of jet vibration (Pedersen), 26.
 Swinton (A. A. C.) See Parsons and Swinton.
- Thermal conductivities of solids, effects of temperature and pressure on.—Part II (Lees), 143.
 Thorpe (T. E.) Bakerian Lecture for 1907.—On the Atomic Weight of Radium, 298.
 Titanic oxide, intimate structure of its crystalline forms (Sollas), 267.
 Townsend (J. S.) The Charges on Positive and Negative Ions in Gases, 207.
 Trajectories of rifled projectiles with various shapes of head (Mallock), 519.
 Trouton (F. T.) and Rankine (A. O.) On the Electrical Resistance of Moving Matter, 420.
 Turner (T.) and Levy (D. M.) The Annealing of Copper : with Special Reference to Dilatation, 1.
 Uranium β -rays, scattering by matter (Crowther), 186.
- Vapour density determination, use of charcoal at low temperatures in (Dewar and Jones), 229.
 Viscosity determinations at high temperatures (Fawsitt), 290.
 Voltmeter, the silver (Smith, Mather, and Lowry), 77.
- Water-colour pigments, action of ozone on (Abney), 146.
 Waves, stationary, non-periodic motion of water moving in (Ayrton), 252.
 Weston cadmium cell, determination of E.M.F. of (Ayrton, Mather, and Smith), 12 ;
 — on the normal (Smith), 75.
 Wilson (C. T. R.) On the Measurement of the Atmospheric Electric Potential Gradient and the Earth-Air Current, 537.
 Wilson (Ernest) Effects of Self-induction in an Iron Cylinder when traversed by Alternating Currents, 369 ; — Winson (V. H.) and O'Dell (G. F.) On the Hysteresis Loss and other Properties of Iron Alloys under very Small Magnetic Forces, 548.
 Wilson (H. A.) The Effect of Hydrogen on the Discharge of Negative Electricity from Hot Platinum, 379 ; — See also Myers and Wilson.
 Wind velocity at 1000 metres and surface-pressure distribution (Gold), 436.
 Winson (V. H.) See Wilson, Ernest.

END OF THE EIGHTIETH VOLUME (SERIES A).



OBITUARY NOTICES
OF
FELLOWS DECEASED.

CONTENTS.

| | PAGE |
|---|---------|
| PIERRE EUGÈNE MARCELLIN BERTHELOT | iii |
| LUDWIG BOLTZMANN | xi |
| AUGUST DUPRÉ | xiv |
| PROFESSOR A. S. HERSCHEL | xix |
| ADMIRAL SIR LEOPOLD MCCLINTOCK, K.C.B., F.R.S.... | xxiii |
| HENRI MOISSAN | xxx |
| WILLIAM HENRY PERKIN... .. | xxxviii |
| H. C. RUSSELL | lx |

PIERRE EUGÈNE MARCELLIN BERTHELOT, 1827—1907.

MARCELLIN BERTHELOT was a native of Paris, born on October 25, 1827, in a flat looking on to the Rue du Mouton, situated in the Place de Grève, now owing to the activity of Baron Haussmann, the Place de l'Hôtel-de-Ville. His father, a doctor of medicine, was a member of the sect of the Jansenists, a small branch of the Gallic Catholic Church. He was a serious man, impatient with the folly of his "concitoyens," and somewhat depressed by the poverty and sufferings of his patients. The "Church of Faith" had its own Liturgy, and the congregation joined in singing psalms and hymns. Many of the "prêtres" were among Dr. Berthelot's patients, and young Berthelot must often have listened to discussions on the attempts, ultimately successful, to substitute the Roman for the Gallic liturgy. Dr. Berthelot was married in 1826, shortly after starting practice. His wife was a lively, bright woman, who transmitted her features to her son.

At that time, Charles the Tenth was on the throne. The allied powers had involved France in a "Gouvernement de Curés"; and it was part of the State Ceremonial to form a procession, which was headed by the Holy Sacrament and the Papal Nuncio, a cardinal in red, from the Tuileries to Notre Dame and back, and in which the King, the Queen, the Dauphin (who, according to Madame Berthelot *mère*, was able to look behind him without turning his head), and the Court took part. The spectators, under the penalty of sacrilege, were obliged to kneel as the Corpus Christi procession passed. Those who refused were prosecuted and severely punished.

Such a travesty of religion was not to Dr. Berthelot's taste; the "bourgeoisie" was liberal and imbued with the sentiments of Voltaire; and the Berthelot family was of the bourgeois class. During the revolutions of 1830 and 1848, their house commanded a full view of one of the chief scenes of operation, and young Berthelot must have often been a spectator of many a scene of disturbance and violence. Highly developed intellectually, and mentally impressionable, his later convictions were doubtless largely owing to his early surroundings.

That Marcellin resembled his mother in features has already been mentioned. But the resemblance was not merely external; there existed between them the most intimate sympathy. Their favourite promenade was in the Bishop's garden behind Notre Dame, along the Quays with their stalls of flowers, and in the Jardin des Plantes. Their minds were both quick and versatile; they were eagerly interested in all that passed around them, and, as Madame Berthelot used to say (borrowing the simile from one of the invasions which she witnessed), they could both "drive a Russian team with a sure hand and at a full gallop." The writer, who knew Berthelot only during his later years—since 1878—never conversed with anyone who possessed such rapidity

of thought. Given an idea, with his quick discursive mind he would follow out all possible paths and by-ways, seeing the consequences of this assumption and of that, interposing occasionally a quaint remark, not exactly humorous, but "*de plaisanterie*." He was a delightful conversationalist, interested and intensely interesting, willing to discuss all possible subjects, and willing, too, to hear all varieties of view, even those contrary to his own opinion.

His persistence, energy of character, and devotion to duty were inherited from his father. Berthelot used to regret that he had not inherited his mother's optimism. He used to say that when a misfortune overtook her, she had what the French call a "*crise de larmes*," soon over, and followed by her usual optimistic cheerfulness; that a rainbow generally rose through her tears, and that she became gaily resigned to the incurable evil.

After the demolition of the Rue du Mouton, the family moved to Neuilly, then quite in the country. Renan often looked in on Sundays as a guest at their midday meal. In one of his private letters he tells how Berthelot and he became friends. He had just renounced his clerical orders, and was "*maitre-répétiteur*" in a school, where he led a lonely and melancholy existence, depressed by the mental struggles which he had come through, and far from his family and his native Brittany. One day, a pupil about four years younger than himself accosted him; the talk became intimate, and a friendship with Berthelot was soon formed, destined to endure for life. Their intercourse was frequent; begun early, when both were slender youths, never a year, hardly a month, passed without their seeing each other. Renan used sometimes to poke fun at Berthelot; the tale is told that, passing a cemetery, Renan said to him: "*Là, voici la seule place que tu n'as jamais convoité.*" Such sallies were always received with amusement and good temper. On another occasion, provoked by the remark that his coat was worn with the air of a cassock, Renan retorted: "*What is there in you, Marcellin, that gives you the air of just having left off fighting behind a barricade?*" While Berthelot retained his slender form, Renan became very corpulent; Berthelot, nervous and active, maintained to the last his almost feverish love of work; Renan was meditative—almost a dreamer. It was Berthelot's sad duty to speak of his lost friend when the monument at Tréguier was raised to his memory. He emphasised Renan's lucidity even to the end, his power of work, his great mental activity; the words were applicable with equal force to himself.

Never was there a more devoted couple than Monsieur and Madame Berthelot. After he had ended his brilliant career at the Lycée Henri IV, Berthelot gained the prize of honour at the open competition in 1846. Without any coaching, he passed successively all his degrees—Bachelier, Licencié, and Docteur-ès-Sciences; for the doctorate he presented a somewhat sensational thesis, entitled, "*The Compounds of Glycerine with Acids, and the Artificial Production of the Natural Fats.*" While working at this research, he was lecture-assistant ("*préparateur*") to Balard, at the Collège de France. In 1861, largely through the influence of Duruy, then Minister of Public Instruction, Berthelot was promoted to the Chair of Organic Chemistry in

that institution ; and there he remained all his life. In that year he was awarded by the Academy of Sciences the Jecker Prize for his remarkable researches on the artificial production of organic compounds by synthesis, and at the same time the Academy recommended the creation of the special Chair which Berthelot filled so long and so illustriously. In his own words : " Adonné, dès mes débuts dans la vie, au culte de la vérité pure, je ne me suis jamais mêlé à la lutte des intérêts pratiques qui divisent les hommes. J'ai vécu dans mon laboratoire solitaire, entouré de quelques élèves, mes amis."

When he won the Jecker Prize, he was in his thirty-fifth year. The appointment to the Chair at the Collège de France made it possible for him to marry Mademoiselle Bréguet, the daughter of a French Swiss, whose family had made money by manufacturing watches, famed since the middle of last century. Monsieur Bréguet was a " constructeur industriel," or builder of factories. He lived near the Place de l'Hôtel-de-Ville, on the Quai de l'Horloge, and the families were acquainted from early days. Mademoiselle was a desirable " partie," well dowered, and of great beauty, which she retained up to the end of her life. She was placid in manner, with lovely eyes, and a brilliant complexion, rendered even more striking, when, at an advanced age, her hair was silver ; and in the church of Saint-Étienne du Mont, there is a picture of Sainte-Hélène, the lovely face of which is taken from a portrait of Madame Berthelot as a girl. The meeting of the young couple was somewhat romantic ; Mademoiselle Bréguet, no doubt, must have appeared to Marcellin to be beyond his reach, and besides, his attention was otherwise occupied. But one day, on the Pont Neuf, Mademoiselle was crossing the longest bridge in Paris in the face of a strong wind, wearing a charming Tuscan hat, then the *mode*. Behind her walked her future husband ; suddenly she turned round, to avoid having her hat blown off, and practically ran into his arms. If not exactly love at first sight, it was a case of love at first touch. Their married life was of the happiest ; indeed, it may be said that they were in love with each other till the end. One of the sons wrote :—" Mon père et ma mère s'adoraient ; jamais le moindre nuage n'avait troublé leur bonheur. Ils s'étaient compris dès le premier jour. Ils étaient si bien faits pour se compléter ! Bien que très lettrée et fort intelligente, maman s'était toujours effacée devant son mari, se bornant à s'efforcer de le rendre parfaitement heureux. C'était, à son avis, la seule façon de collaborer à son œuvre." Another intimate friend added :—" Monsieur et Madame Berthelot s'adoraient ; tous deux étaient de la nature d'élites ; sa compagne n'avait cessé de l'encourager et de le soutenir." No one visiting their house could fail to remark this absolute devotion to each other ; never was there a happier family. Although not a conversationalist, Madame Berthelot, by her perfect tact, her serene manner, and her charming sympathetic face, knew how to make each guest appear at his best ; the ball of conversation was lightly tossed round the table, Berthelot himself, by his quaint and paradoxical remarks, contributing his share. A dinner at Berthelot's, in his old house in the Palais Mazarin, the home of the Institute, was a thing to be remembered.

Always charitably disposed, Madame Berthelot used to send all the cast-off clothes of the family to the cleaners, and after they had been carefully mended, they were distributed to poor friends.

In 1881, Berthelot was elected a "Permanent Senator"; he thought it incumbent on him to bear his share in the Government of his country. With his wife's help, he managed to carry on his two functions at the same time. In his place in the Senate, Berthelot used to sit buried in his arm-chair, his head thrown back, and his eyes closed, apparently inattentive to all that passed; but nothing of importance escaped him. He took a leading and active part as member of various Committees dealing with education, and in 1886, as Minister of Education in the Goblet Cabinet, he busied himself with the reform of educational methods in such a manner as to acquire a wide popularity; the Bills introduced by him dealt with primary and with higher instruction, with universities, and with technical schools; in the last he was no believer, except in so far as manual training was given. Later, in 1895, he was for a short time Foreign Minister in the Bourgeois Cabinet; but the delays of parliamentary procedure were not to his mind. It was with difficulty that he was persuaded to sign the Anglo-French Treaty defining the position of Siam; and, almost immediately after, he resigned office.

Berthelot's career is easily told; it consisted of honour after honour. He was elected a Member of the Académie de Médecine in 1863, and in 1867 he collaborated in the foundation of the École des Hautes Études, and in the reorganisation of scientific teaching. Membership of the Académie des Sciences followed in 1873, and in 1889 he became its *Sécrétaire Perpetuel*.

In 1900, he had the rare honour of being elected among the immortal forty in the Académie Française, succeeding to the Chair of Joseph Bertrand. Of 28 voters, 19 voted for him, 9 abstaining. Four years later, in 1904, he delivered the statutory discourse. He was a Member of the *Conseil Supérieur des Beaux-Arts*, of the *Conseil Supérieur de l'Instruction Publique*, and in 1886 he was created a Grand Officier of the Legion of Honour. He was Foreign Member of almost every scientific society in the world, including our own Royal Society.

On November 24, 1901, the Berthelot jubilee celebration, the anniversary of his seventy-fifth birthday, was held in Paris, M. Loubet, President of the Republic, in the Chair. It took place in the great hall of the Sorbonne; all the Cabinet, the Ambassadors of all countries, and delegates from universities and scientific societies from all over the world were present. Madame Berthelot with her children and grand-children occupied a conspicuous place, beaming over with unaffected pleasure; Berthelot had declined the State offer to make a triumphal procession in the carriage of the President with a military escort; he went on foot from the Quai Voltaire to the Sorbonne, his greatcoat buttoned so as to hide the grand-cordon of the Legion of Honour, and his head down so as to avoid recognition. He was embraced by the President of the Republic, and amid the enthusiastic applause of the spectators, address after address was delivered, each delegate conveying the congratulations of the body which

he represented. It was a national fête. Thus did the French honour science and its *doyen*.

On March 18, 1907, the end came. Madame Berthelot had been ailing for about three months; it turned out to be an attack of heart-disease, dangerous at the age of seventy. After she was confined to bed, Berthelot watched by her each night, seated in a deep arm-chair, only leaving her when she was asleep. He himself suffered from the same disease, and it was accelerated by his want of rest. His family noticed his feverish appearance in the mornings; he excused himself by saying that he was finishing a memoir for publication. On Passion Sunday there was a slight improvement, and Berthelot passed the afternoon in his laboratory at Meudon. That night, however, Madame Berthelot became comatose, and her husband never left her bed-side until Monday at four, when the end came. Berthelot suddenly rose from the arm-chair in which he was seated, threw his arms in the air, uttered a cry, and fell back dead. They died, as they had lived, together.

It now remains to give a sketch of Berthelot's scientific work. The "Prix-Jecker" has already been alluded to. This was the reward of his labours on the synthesis of carbon compounds. He began in 1851 by investigating the action of a red-heat on alcohol, acetic acid, naphthalene, and benzene; this led him in 1860 to the rediscovery of acetylene, a compound originally obtained by Edmund Davy, Sir Humphry's brother. In 1856, he synthesised methane by the action of a mixture of sulphuretted hydrogen with carbon disulphide on copper; and in 1862 he obtained ethylene and acetylene by heating marsh-gas to redness. His condensation of acetylene to benzene in 1866 established the first link between the fatty and the aromatic series. His direct synthesis of acetylene from carbon and hydrogen in 1862, and the formation of alcohol by hydrolysing ethyl-sulphuric acid, obtained by absorbing ethylene in sulphuric acid, taken in conjunction with his synthesis of hydrocyanic acid in 1868, pointed the way to the formation from the elements of innumerable complicated compounds of carbon.

Much light has also been thrown by Berthelot on the alcohols. In 1857, he produced methyl alcohol from marsh-gas by chlorination and hydrolysis; in 1858, he recognised cholesterine, trehalose, meconine, and camphol as alcohols; in 1863, he added thymol, phenol, and cresol to the same class; and he showed how to diagnose alcohols by acetylation.

Turning to the esters, the nature of glycerine occupied his attention in 1853; in that year he succeeded in synthesising some animal fats, and showing their analogy with esters, as has already been mentioned; and he prepared other salts of glyceryl by submitting it to the action of acids. The action of hydriodic acid was, however, found to yield two substances of a different nature, namely, isopropyl iodide, and allyl iodide; and from the latter, he prepared, for the first time, artificial oil of mustard. The analogy of sugars with glycerine led him to investigate the action of acids on sugars, and this resulted in the synthesis of many of their esters. The fermentation

of mannite and other polyhydric alcohols was also studied in 1856 and 1857; also the conversion of mannite and glycerine into sugars, properly so called. The esters of pinitic acid, with tartaric acid, were also studied, and in 1858, trehalose and melezitose were discovered. In 1859 Berthelot maintained that the action of yeast is not a vital, but a chemical phenomenon; and he returned again and again to the study of fermentation.

These and other similar investigations on esters led him, in conjunction with Péan de Saint-Gilles, to investigate the rate of esterification; and the experiments, begun in 1861, led to a long piece of work on chemical equilibrium, and on "affinity." In 1869 he attempted to limit the action of hydrochloric acid on zinc by pressure, but unsuccessfully; and in the same year he investigated the equilibrium between carbon and hydrogen, in sparking acetylene under pressure. And later in that year he announced laws, describing the partition of bodies between two solvents, and he investigated the state of equilibrium in solution. In the same year appeared the first of the long series of researches on thermal chemistry. In 1875 he returned to the subject of chemical equilibrium, dealing with the partition of acids between several bases in solution.

Among other syntheses was that of formic acid from caustic soda and carbon monoxide; oxalic acid was produced by the oxidation of acetylene; and acetates, by the slow oxidation of acetylene, in contact with air and caustic potash, in diffuse daylight.

In 1857 the combination of unsaturated hydrocarbons with the halogen acids was studied, as well as the conversion of chloro- and bromo- hydrocarbons into hydrocarbons by reduction. In 1860 ethyl iodide was synthesised by the union of ethylene with hydriodic acid; and in 1867 the use of a concentrated solution of hydriodic acid as a universal reducing agent at high temperatures was discovered.

Berthelot's numerous and important researches on the acetylides of silver and copper doubtless led him to pay attention to explosives. Begun in 1862, they were continued until 1866; and in that year he enunciated the theory that the production of mineral oils may conceivably have been due to the action of water and carbonic acid on acetylides of the alkaline metals, and to the subsequent resolutions of acetylene at a high temperature into other hydrocarbons. These researches on the acetylides were followed in 1870 by investigations on the explosive force of powders, the explosions being carried out in a calorimeter.

In 1871 Berthelot proceeded to investigate the detonation of mixtures of gases, and he made measurements of the heat of formation of nitro-glycerine. In 1874 and 1876 the work was continued; and in 1877 it was extended to the temperatures of explosive mixtures, and to the velocity of combustion. In 1878 explosive mixtures of dust with air, and in 1880 fulminating mercury, were examined. A research on the velocity of the explosive wave in gases followed in 1882; and in 1884 measurements of the specific heats of gases at high temperatures were made. In the same year the calorimetric

bomb was invented; and in 1892 it was adapted to the requirements of organic analysis.

Allotropic varieties of the elements also claimed Berthelot's attention. In 1857 he commenced with a study of allotropic varieties of sulphur; and in 1870 he investigated these varieties thermally. In 1869 he examined the allotropic varieties of carbon, and this led him to the preparation of various forms of graphitic oxides. Allotropic silver and other allotropic forms were also the subject of his research.

Berthelot also did much work by help of the "silent discharge." Attracted to it in 1876, when he submitted mixtures of organic substances with nitrogen to its influence, and succeeded in causing the nitrogen to enter into combination, he repeated Brodie's experiments, and reproduced the oxide C_4O_3 . In 1878 he produced by the same means the higher oxide of sulphur, S_8O_7 , in needles often a centimetre in length, and in 1881 pernitric anhydride. In 1895 he carried out similar work with argon, and later with helium.

From an early date, Berthelot interested himself in agricultural chemistry. From his laboratory at Meudon, assisted by his colleague, André, have appeared a succession of memoirs, chiefly relating to the absorption of nitrogen by plants, and to their behaviour under the influence of electric energy. To the very end his interest was kept up in these experiments; and he was hopeful of increasing by electrical means the productiveness of cereals, and of adding to the world's food-supply.

Though so keenly alive to the present, the past had for Berthelot a great attraction. In 1877 he analysed a sample of Roman wine, which had been preserved in a sealed flask; and he has contributed to the *Journals* many notices of the composition of ancient objects of metal. His works on "*Les origines de l'Alchimie*," and on a "*Collection des anciens Alchimistes grecs, texte et traduction*," and his "*Introduction à l'étude de la Chimie des Anciens et du moyen âge*" involved long research of ancient manuscripts; he acquired facility in reading ancient Greek, though for Arabian sources he was dependent on others.

Berthelot was the author of numerous works besides those on Alchemy. In 1872 he published a *Treatise on Organic Chemistry*; a fourth edition appeared in 1899. This was followed by "*La Synthèse chimique*"; "*Essai de Chimie mécanique*" (1879), in which he announced the principle of "maximum work," a doctrine afterwards withdrawn, or, at least, greatly modified in 1894; "*Traité pratique de Calorimétrie chimique*" (1893); "*Thermochimie: Données et lois numériques*" (1898), in which an account of his long series of calorimetical measurements is given; this work and that of Julius Thomsen on "*Thermochemie*" are the standard books on the subject, and each contains the results of the individual researches of its author.

Berthelot's mind was one which interested itself greatly, not merely with things, but with their origins; and in "*Science et Philosophie*"

and "Science et Morale" he treats of the relation of science to human thought. The same critical spirit manifests itself in his "Histoire des Sciences: La Chimie au moyen âge," in which Syrian and Arabian Alchemy is treated of.

A partisan of Lavoisier, "La Revolution chimique de Lavoisier" presents that point of view strongly. He also published his correspondence with Renan in 1898.

The lectures which he delivered at the Collège de France were published under the titles "Leçons sur les Méthodes générales de Synthèse en Chimie organique"; "Leçons sur la thermochimie"; "Leçons sur les principes sucrés"; and "Leçons sur l'isomérisation." The application of thermal chemistry to problems of life was treated of in his "Chaleur animale," and in 1901 he published three volumes on "Les Carbures d'Hydrogène."

One point remains to be mentioned. It has sometimes been objected that Berthelot kept science on a wrong path by persistently retaining the old system of representing formulæ, after all the rest of the world had abandoned it. The writer remembers well a conversation in the late '80's, in which Berthelot defended his views. He thought the position of those who employed the customary notation (and, of course, they comprised practically the whole chemical world) not unlike that of the defenders of the phlogiston theory! The retort was obvious, but not made. Berthelot had not even the excuse of Cavendish, who after a calm deliberate statement of the results of his research in terms of the then new hypothesis of Lavoisier re-stated it in terms of the phlogistic method, saying that he preferred to make use of the older and better known language, rather than of the newer modes of expression. For in 1890 Berthelot was, perhaps, the only survivor of the older chemists. Professor Guye, who attended his lectures in 1890-91, tells that the session was begun, as usual, with the special notation of which Berthelot was the sole defender ("equivalents based on two volumes of vapour"), and that, without the slightest warning, in the middle of a "chapitre," to the great astonishment of his audience, he effected the change, dealing with a subject of which the first portion had been expounded in the "equivalent" notation, and continuing in the newer notation of which he had so long been the opponent.

No one is more conscious than the writer that he has failed to do justice to this remarkable personality. His only excuse is that he has done his best. He wishes that it were possible to convey to the reader a sense of the brilliancy, the vivacity, the power, the ability, the talent, and the high character of the great chemist. In the life-like plaquette by Chaplain, his features and his attitude have been admirably reproduced. Truly he was one of the most remarkable of the eminent men of whom France may be proud. He and his wife lie in the vaults of the Pantheon, in life united, in death not put asunder.

W. R.

LUDWIG BOLTZMANN. 1844—1906.

LUDWIG BOLTZMANN was born on February 20, 1844, and was the son of Ludwig Boltzmann, Fin.-Bez.-Kommiss., and Katherina Paurenfeind. He was educated at the Gymnasium at Linz, from whence he proceeded to the University of Vienna. He appears to have been early attached to the study of molecular mathematical physics, for his paper, "Ueber die mechanische Bedeutung des zweiten Hauptsatzes der Wärmetheorie," was read on February 8, 1866, and was thus written at the age of 21. Boltzmann obtained the Doctorate, and became Privat-Dozent, and in 1867 was appointed Assistant in the Physical Institute of the University of Vienna. This Institute, where much of Boltzmann's best work was done, was a large and dingy-looking house in the Türkenstrasse, and formed a striking contrast to the palatial edifices without which no physical department is content nowadays. But, if the bricks and mortar looked uninviting, the brains inside more than made up for the deficiency. In or before 1875, Boltzmann became corresponding member of the Vienna Academy of Sciences, and, about a year later or thereabouts, he obtained a chair at the University of Graz, where he remained till about 1891. In 1876 he married Henrietta von Aigentier, and in 1885 he was promoted from corresponding to ordinary membership of the Vienna Academy. In 1891 he was called to fill a vacant chair at Munich, and four years later was appointed Professor of Physics at Vienna. In 1904 he was called to Leipzig. He was not happy in the new surroundings, and the longing to return to his old University resulted in his stay at Leipzig being an extremely short one—a matter of a few months, we believe. In addition to the duties attaching to the Chair of Physics, the authorities placed a course of outside lectures in his hands, and with this and other work he was able to earn an income of about £800 a year. His election as corresponding Fellow of our Society dates from 1899.

In estimating the value of Boltzmann's work in that branch of mathematical physics with which his name is so intimately associated, it would be a difficult and unproductive task to discuss claims of priority on mere matters of details. The groundwork of the Kinetic Theory of Gases, and in particular the opinion that temperature is a quantity of the same kind as molecular kinetic energy, had of course remained buried in the manuscript of Waterston long before Boltzmann's first paper was published. But while others were working side by side with Boltzmann during a great part of the time that he was publishing his best work, it cannot be said that this concurrence in any way lessened the importance of Boltzmann's work. It is certain that his first paper on the Second Law antedates by several years the first of the Clausius-Szily series of papers on the same subject. If Boltzmann's original proposal to establish that law on a purely deductive basis, and to penetrate beyond the inevitable assumption, which seems to

present itself at every step as a bar to further progress, formed the work of a lifetime, certainly Clausius and Szily did not do much, if anything, in attempting to unearth and, if possible, root out the assumption in question. In fact, the assumption underlying the Second Law has been a stumbling block and at the same time a stimulus to progress which has played much the same part in the development of statistical thermodynamics that Euclid's axiom has played in the development of geometry.

In the first place the notion of temperature leads to the conception of a law of partition of energy. Boltzmann was not long in following up in the direction started by Maxwell, and his criticisms and further developments, leading in turn to further work from the pen of Maxwell—Boltzmann was only 24 at the time—must be regarded as striking achievements on the part of two young physicists of that period. Next comes the difficult question of irreversibility, and in the theorem known as Boltzmann's Minimum Theorem we have a remarkable contribution indeed. If any element of chance is assumed to enter into the question of molecular motions, this theorem establishes a definite tendency to a state of energy equilibrium. That it does not dispense with the inevitable assumption is shown by imagining the motion reversed. It is true that this would lead to a highly improbable hypothesis, namely, that the probability of a collision between two molecules depended on their motions after instead of before collision. But even so, the matter is not a question of pure particle dynamics. Later discussions of the minimum theorem viewed in the present aspect have led to an output of much good work on the part of Boltzmann.

A fresh line of thought was opened up by an idea previously suggested by Dr. Oskar Emil Meyer in the application of the theory of probability to problems of statistical dynamics. Boltzmann proved that in a molecular dynamical system if for a single molecule all values of the coordinates and corresponding momenta are *a priori* equally probable, then the most probable distribution in an aggregate consisting of a large number of molecules is the well-known Boltzmann-Maxwell distribution. He also established relations between the probability function and entropy. This method of investigation was applied quite recently to quite a different purpose, namely, the irreversible problems of radiation, by Planck, and, though Planck's book has only been out a short time, it has already received discussion at the hands of Dr. Paul Ehrenfest, of Goettingen. The publication of Helmholtz's paper on monocyclic systems gave Boltzmann another method of attack, and led to a detailed examination of the conditions that a system should be "statistically monocyclic," a point of view which does not seem to have been foreshadowed to any great extent by Helmholtz.

Of other subjects on which Boltzmann wrote, we need only refer to his lectures on Maxwell's electrical and optical theories, his studies of the Lagrangian equations for non-holonomic systems, and his papers on Hertz's experiments.

Boltzmann attended the British Association at Oxford in 1894, and was

also present for a short time at the Southport Meeting in 1903, and many English workers were thus brought into personal touch with the Vienna physicist. His visit to Oxford will long be remembered. He was greatly struck with the reception accorded him and, in returning thanks for the foreign guests, he expressed a wish to "often come at England."

Since Boltzmann first came to the front the trend of physical thought has shifted from molecules to the ether, and from the ether to electrons. We have thus come back to kinetic theories, and have merely extended the order of smallness of the particles of which these theories take cognisance. But, while students of reversible phenomena have had fairly straightforward problems to solve, the problem of irreversibility still remains to a great extent a mystery, and nobody seems as yet to have got to the bottom of it. The irreversible phenomena of the universe all have a certain definite trend, and lead to the transformation of energy into certain definite forms. We say that certain forms of energy are less available than others, but why the less available forms are those associated with what are commonly called heat phenomena is a riddle which Boltzmann went far to solve, but which still presents difficulties.

In 1904, on the celebration of Boltzmann's sixtieth birthday, physicists in all parts of the world worked together to honour the occasion by producing as a *Festschrift* a monumental volume dealing with every aspect of physical thought.

The news that Boltzmann had committed suicide while away on his summer holiday last August came as a terrible shock to those who knew him. Of the details of the incident the present writer knows nothing, but surely it suggests several serious reflections. Is it not probable that Boltzmann's ever-active brain had been taxed too heavily by the difficult and elusive problems which he was endeavouring to solve? Mathematical research is a dangerous occupation if carried too far, and the consequences that may have been the result of this intense concentration of thought should prove a warning to others not to allow themselves to be too deeply absorbed in any particular investigation. The difficulty of tearing oneself away from a particular line of work till it has been finished constitutes a grave danger. There are few mathematicians and physicists who would not gladly accept life-fellowships that would enable them to devote their whole time to research, but would they live to do their best work under such artificial conditions? It may be that such obstacles and difficulties as the necessity of undertaking some elementary teaching constitute an analogue to the refrigerator which is necessary for the continuous and efficient working of a thermodynamic engine.

Boltzmann leaves behind him four children, and when last the present writer visited him at Vienna in 1903, his eldest son and daughter were studying for the University. It need hardly be added that the honorary title of Hofrat was conferred on him by the Austrian Government.

G. H. B.

AUGUST DUPRÉ, 1835—1907.

AUGUST DUPRÉ was born at Mainz on September 6, 1835, and died at his residence, Mount Edgumbe, Sutton, Surrey, after some weeks' illness, on July 15, 1907, in his seventy-second year. He was the second son of J. F. Dupré, a merchant and citizen of the then Freie Reichsstadt of Frankfurt-am-Main, and his birth was entered in the register of the "Freie Französische Gemeinde" of that city. On his father's side Dupré traces his descent in a direct line from Cornelius Dupré, a French Huguenot who left France in 1685, after the suspension of the Edict of Nantes, and settled in the Palatinate, and who distinguished himself later as an officer in the army of Prince Eugene. Dupré's mother was also of Huguenot descent. His family was, therefore, originally French, but by intermarriage had become practically German in the course of a hundred and fifty years.

Dupré had a somewhat varied school education which he completed at the Polytechnic schools of Giessen and Darmstadt, and entered as a student of the University of Giessen in 1852, at the age of seventeen. There he studied chemistry under Professor Will, also attending the lectures of Kopp and others. From Giessen he proceeded to Heidelberg in 1854, Bunsen and Kirchhoff being among his teachers, and there he finally took his degree of Doctor of Philosophy in 1855, being barely twenty years old. It is interesting to note that fifty years later, in 1905, the University renewed his Diploma (Goldenes Doctor-Jubiläum) in recognition of his scientific work. Among his fellow students at Giessen and Heidelberg who became famous in later life were Harley, Matthiessen, Roscoe, and Volhard.

In the autumn of 1855 Dupré proceeded to London and became assistant to Odling, whom he accompanied to Guy's Hospital, remaining with him till 1863.

In 1864 he was appointed Lecturer on Chemistry and Toxicology at the Westminster Hospital Medical School, in succession to his elder brother, Dr. F. W. Dupré, who had given up the appointment in order to take up mining in the then recently discovered salt deposits of Stassfurt, in connection with which he is now so well known.

August Dupré remained in London for the rest of his life, and became a naturalised English subject in 1866. He resigned his appointment at the Westminster Medical School in 1897, after thirty-three years' tenure, but during the last ten years, owing to pressure of consulting work, he had practically handed over the lectureship to the writer, who was associated with him as Assistant-Lecturer from 1885. From 1897 till his death in 1907 he continued to practise as consulting chemist, both privately and in connection with several Government Departments, at his private laboratory in Edinburgh Mansions, Westminster.

Soon after he left the University Dupré began to publish various scientific papers and, owing doubtless to this fact and the reputation for ability which he enjoyed in his own immediate circle, it was not long before he obtained several other public appointments in addition to the lectureship at Westminster.

Thus in 1871 he was appointed Chemical Referee to the Local Government Board and about this time he was first consulted by Sir Vivian Majendie, then Colonel Majendie, Chief Inspector in the Explosives Department of the Home Office, to which Department he shortly after became permanently attached as Consulting Chemist. In 1873 he became Public Analyst for Westminster, which post he held till 1901. In 1874 he was appointed Lecturer on Toxicology at the London School of Medicine for Women, an appointment in which he always showed the keenest interest and which he held till 1901.

He was also consulted by the Board of Trade, the Treasury and the late Metropolitan Board of Works.

In all these appointments and consultations he may be said to have distinguished himself brilliantly, by his rapid and thorough grasp of the problems in hand, his marked originality, his extreme conscientiousness, his intense enthusiasm, and his infinite capacity for taking trouble. He rapidly rose to eminence.

In 1875 he was elected a Fellow of the Royal Society. In 1877 he became President of the Society of Public Analysts. From 1871 to 1874 he sat on the Council of the Chemical Society. In 1885 he was made a Vice-President of the Institute of Chemistry. In 1886 he was elected Examiner in Chemistry to the Royal College of Physicians, and again in 1892.

In 1888 he was appointed a Member of the War Office Committee on Explosives, in 1891 an Associate Member of the Ordnance Committee, and in 1906 a Member of the Ordnance Research Board.

His earlier work for the Local Government Board, beginning in 1871, was largely analytical, but in 1884, 1885, and 1887 he made a series of investigations in connection with the purification of water supplies by aëration and by the agency of bacteria, which must certainly rank as original researches of high merit and which undoubtedly have assisted greatly in the evolution of the most modern methods of treating sewage. They are published in the Medical Officers' Reports of the above dates, but are probably not widely known in the present day.

In conjunction with Abel, Dibdin, Keates, Odling, and Voelcker he advised the late Metropolitan Board of Works as to the condition of the Thames in 1878, 1882, and 1883, and in 1884 made numerous experiments in conjunction with Mr. Dibdin on the treatment of London sewage on a large scale. This work is referred to at great length in the Report of the Royal Commission on Metropolitan Sewage Discharge in 1884. He was a Member of the Departmental Committee on White Lead in 1893, and gave evidence before numerous other Royal Commissions.

Of all this Government work it was the Home Office appointment which mainly occupied him. When, in 1871, he was first consulted by the Explosives Department, the manufacture in England of dynamite and guncotton had but recently commenced, and these two were practically the only high explosives known at that time. Much had to be done on the part of the Government in connection with the safe manufacture, storage, transport, and use of these explosives, and the rapid development of the industry necessitated the introduction of the Explosives Act of 1875. In 1876 the authorised list of explosives comprised twelve kinds only, but in 1907 it had risen to 182. In addition, during this period, 108 explosives had been passed by the Home Office after examination by Dupré, and over one hundred had been rejected by his advice. He thus investigated, during a period of thirty-six years, nearly four hundred entirely new explosives of the most varied composition, and further examined, at frequent intervals, all explosives imported into England, as to safety. In the course of this work he had often to evolve original methods of analysis or of testing for safety, and in this latter direction, especially, he rendered great services to the Government, and, indirectly, to the public.

It was also part of his duty to assist H.M. Inspectors in investigating the causes of various accidental explosions in factories and elsewhere, which occurred from time to time. His work, therefore, involved heavy responsibilities, and sometimes serious personal risks, notably during the Fenian outrages in 1882-83, when he had to examine several "infernal machines," and on the occasion of the Birmingham scare in 1883, when he superintended and himself assisted in the conversion of several hundred pounds of impure nitro-glycerine (which had been secretly manufactured in the heart of Birmingham) into dynamite, and so averted what might have been a terribly disastrous explosion. He was highly commended in the House of Commons by Sir William Harcourt, then Home Secretary, in connection with this "prompt and courageous action," and by Sir Vivian Majendie in the 8th Annual Report of the Inspectors of Explosives, in 1883. As late as 1907 he devised a new method of testing for infinitesimal traces of mercury in explosive compounds. His private consulting work was also considerable, and he was engaged in many important law cases as a scientific witness.

It might well be supposed that these responsible undertakings engrossed him entirely, but this was far from being the case. During the first twenty years of his appointment at the Westminster Hospital Medical School he gave great attention to his lectures and to the practical teaching of chemistry. His lectures were always very fully illustrated with experiments which year after year seemed to give him renewed pleasure to perform, and although not very easy to follow, he was always extremely interesting owing to the mass of information he had ever ready to hand. In 1886 he published, in conjunction with the writer, then recently appointed Assistant-Lecturer, "*A Manual of Inorganic Chemistry*," which had some success, and which reached its third edition in 1901. This book was dedicated to Professor Will, of

Giessen, whom he always spoke of with the highest admiration and reverence as a great teacher.

The subject of toxicology, on which, as already said, he also lectured both at Westminster and at the London School of Medicine for Women, had always specially interested him, and he became known and was not unfrequently consulted as a toxicologist. He was brought into particular prominence in connection with the celebrated Lamson case in 1881.

As an instance of the thoroughness of his work, the writer well remembers Dupré tasting sixteen quinine powders which had been prepared for the unfortunate victim in this case, and his almost immediately experiencing the now familiar and somewhat alarming physiological effect of the aconitine which he found in the last powder. He was associated in this case with Sir Thomas Stevenson.

It has already been mentioned that very soon after leaving the University Dupré began to publish scientific papers, and it seems surprising that amid such varied occupations he found time to work out so many original problems. His papers amount to no less than thirty-four in number between 1855 and 1902. Of these, five papers are included in the Proceedings and Transactions of the Royal Society between 1866 and 1872. The first, in 1866, with Dr. Bence Jones, on "Animal Quinoidine," may be said to have anticipated the later important researches of Selmi and others on Ptoamines. Another, in 1871, dealt ably with the Elimination of Alcohol in the human subject, a problem then arousing much interest. The remaining four papers, published between 1868 and 1872, some of the work being done in conjunction with the late Mr. F. J. M. Page, rank, perhaps, as his best efforts, treating of the Specific Heat and other characters of various aqueous mixtures and solutions, notably of mixtures of ethylic alcohol and water, in the course of which he made the remarkable observation that mixtures of these last two substances up to 36 per cent. ethylic alcohol had a specific heat sensibly higher than that of water itself.

In the Journal of the Chemical Society are found eight papers between 1867 and 1880. One on the Synthesis of Formic and Sulphurous Acids, four on the Various Constituents of Wine, including compound ethers, one on the Estimation of Urea with Hypobromite by means of an ingenious apparatus now so universally employed, and two, in conjunction with the writer, on a New Method of Estimating Minute Quantities of Carbon, which was included by the late Dr. E. Frankland in his well-known work on Water Analysis.

Between 1877 and 1883 he read no less than thirteen papers before the Society of Public Analysts, dealing with the analysis of foods or water, and most of the methods evolved by him in these publications are still used or have given rise to improved operations, notably those dealing with butter fat, fusel oil in whiskey and other spirits, alum in flour and bread, foreign colouring matters in wine, and methods of water analysis.

He published only two papers on Explosives, to which he had given such

great attention, before the Society of Chemical Industry, and these as late as 1902. As a matter of fact, however, much original work was done by him in this branch of chemistry, some of which appears in the Annual Reports of H.M. Inspectors of Explosives, while again much could not be put forward owing to his official connection with the Home Office.

His earliest papers, published between 1855 and 1862, are six in number, and deal with volumetric methods and spectrum analysis (conjointly with his brother, Dr. F. W. Dupré), the iodic test for morphia and the presence of copper in plant and animal tissues, this last in conjunction with Odling.

To the chemistry of wine, as will be seen from the above summary, he devoted a good deal of attention, and was joint author with Dr. Thudichum of a work entitled "On the Origin, Nature, and Varieties of Wine," published in 1872, in which a considerable amount of original analytical work is embodied.

Dupré married, in 1876, Miss Florence Marie Robberds, of Manchester, and leaves a family of one daughter and four sons, two of whom, Frederick and Percy, are now carrying on his work for the Home Office. He was of a striking personality, of medium height, but very powerfully built, with a massive head and brow, and must have possessed an iron constitution. As a young man he was a skilled fencer and swimmer. He was of somewhat excitable temperament, but had a most kindly disposition. Although not a fluent speaker, he was impressive from his obvious sincerity, and the thorough knowledge he displayed. He therefore made an excellent expert witness, and was more than once complimented in Court on his straightforward evidence. In controversy he was unsparing where facts were concerned, and at times intensely sarcastic.

Although almost wholly devoted to chemistry, his mind found many other outlets. He was a great student of history, and his quite remarkable memory was frequently exemplified in conversation on this subject. He was also exceptionally well read in general as well as in scientific literature, both English and German, and amassed a large collection of books. Among other hobbies he pursued astronomy and photography. His mind, indeed, seems rarely to have been idle, he had a perfect passion for work and, except for a few weeks' holiday annually, he never relaxed. There is little doubt that at one time, about 1891, he overstrained his brain, and was obliged for some months to take a complete rest, which, fortunately, restored him to renewed energy. Like many great men, he was of a modest and retiring nature, and probably but few of his contemporaries have realised the magnitude and variety of the work he accomplished during fifty years of almost unceasing activity.*

* The Royal Society is indebted for this obituary notice to the kindness of Dr. H. Wilson Hake, who succeeded Dr. Dupré in the Chair of Chemistry at the Westminster Hospital Medical School.—Sec. R.S.

PROFESSOR A. S. HERSCHEL, 1836—1907.

To Sir John Herschel (1792—1871), the only child of Sir William Herschel (1739—1822), twelve children were born, three sons and nine daughters. Alexander Stewart was the fifth child and the second son. He was born during the historical visit of his father to the Cape of Good Hope in 1836, and the bare facts about his life and work may here be given in his own words, from a document preserved among his papers and apparently intended for such use. The careful method of statement in regard not only to the details of his career but also to the document itself—*e.g.*, that it was a “first” copy, and that the label did not extend beyond a “single page”—is thoroughly characteristic of his work and writings. To complete the record, it must be added that he continued to live at Observatory House, Slough, until his death on June 18, 1907; and that he joined the Société Astronomique de France in March, 1897.

First copy of (single page) “Record” label and signature and date, gummed on back of enlarged carbon print “Museum” portrait (by Melhuish), presented to the South Kensington Museum, 1893, by the Amateur Photographic Association :—

Alexander Stewart Herschel.—Second son of the late Sir John F. W. Herschel, Bart. Born in Cape Colony in 1836, and educated at Clapham Grammar School (1851—55) by the late Professor of Astronomy of Oxford University, the Rev. C. Pritchard, F.R.S., etc.; and at Trinity College, Cambridge (1855—59), and at the Royal School of Mines, London (1861—2—(1865 ?)). B.A. Camb., 1859; M.A. Camb. and (*ad eundem*) Durham, 1877; Hon. D.C.L. Durham, 1886. Became Fellow R.A.S., 1867; Assoc. Liverpool Astronomical Society, 1888; Honorary Member of the North of England Institute of Mining and Mechanical Engineers, 1871 (united in 1889 to the Federated Institute of Mining Engineers), and of the Newcastle-on-Tyne Chemical Society (united in 1883—4 to the Society of Chemical Industry), 1871; Corresponding Member of the Philosophical Society of Glasgow, 1874; F.R.S., 1884; Member of the Physical Society of London, 1889; Life Member of the British Association, 1871; and of the Society of Arts, 1892. Was Lecturer on Natural Philosophy and Professor of Mechanical and Experimental Physics in the Andersonian University of Glasgow, 1866—71; and Professor of Physics and Experimental Philosophy in the University of Durham College of Science, Newcastle-on-Tyne, 1871—86; and Honorary Professor of that Institution since 1886.

Writer of the Reports of the British Association on Luminous Meteors and on the Thermal Conductivities of Rocks, 1861—81; and of various papers

relating to Meteors, Meteorology, and Physics in Societies' Proceedings, and in Scientific Journals since 1860.

Present Residence: Observatory House, Slough.

Ipsæ Scripsit, September 14, 1893.

A. S. HERSCHEL.

Of the Clapham school days of Alexander and his brothers a brief note or two have been preserved in the "Memoirs of Professor Pritchard." (A letter written in 1844 refers to the eldest brother, now Sir William J. Herschel.) And in correspondence with Sir John in later years, Pritchard several times refers to his old pupils: *e.g.*, in 1866 he was anxious that Alexander Herschel should undertake the "preparing the catalogue of Sir William Herschel's double stars for publication in the 'Transactions of the R. Ast. Soc.,'" and it seems probable that this plan was carried into effect, though in the printed paper (Mem. R.A.S., vol. 35) Sir John Herschel makes no allusion to his son's help.*

Alexander Herschel was best known for his work on luminous meteors: and due prominence is accorded to this work in his own concise record above given. He was himself a diligent observer, spending long hours in the open in the watch for meteors. His post of astronomical observation at Slough was necessarily different from that of his grandfather: for during the half-century following the death of Sir William, trees had grown up in the garden where his great telescope used to stand; and when four of his grandchildren returned to Observatory House in 1888 (after half a century of occupation by strangers), they found a pleasantly shaded garden, but no horizon visible. Over the wall however, in the kitchen-garden, where Sir William's forges and optical works used to be, there were no trees; and there Alexander Herschel would lie on his back and watch the broad sky for meteors. His observations are contained in a long series of small note-books, and every observation is numbered, starting each new year with unity again. The last observation is dated 1907, February 13. A hasty glance at these books with unskilled eyes suggests that probably there is a great deal of valuable material of which no use has yet been made. But a proper estimate of the value of his work in this field can only be given by a meteor observer; and Mr. W. F. Denning has very kindly written the following notes for inclusion in this notice:—

"Professor Herschel's meteoric work was characterised by its remarkable accuracy, its comprehensive detail and large amount, extending over something like half a century. It not only embraced his personal observations, but comprised the comparison and reduction of a great number of materials sent in to him by various other observers in England and abroad. During a long series of years he collected as many descriptions as possible of the fire-balls which appeared from time to time, and calculated their real paths in the atmosphere. Some of the very extensive results which he obtained were

* The point has been very kindly verified from a bundle of MS. computations by Miss Herschel.

published in the Proceedings of the Meteorological Society, Annual Reports of the British Association, Monthly Notices, and Journal of the British Astronomical Association. In determining the real paths of meteors, Professor Herschel frequently had conflicting material to discuss, but no one was so eminently well fitted as he was to investigate such results and base correct deductions upon them. His long experience and sound judgment enabled him to deal effectively with data which another computer would be inclined to reject altogether as incompatible and irreducible.

"As regards Professor Herschel's own observations, chiefly made at Hawkhurst, in Kent, Newcastle-on-Tyne, and Slough, he amassed a very considerable number, and fixed the radiant points of many of the showers to which they belonged, but we believe that he did not publish any complete list of the radiants which he observed from time to time. A number of them, however, were referred to in fragmentary form in one or other of the scientific journals published soon after the observations were made. As a result of long practice, he acquired great precision in noting the flights of individual meteors amongst the stars, and could reproduce them on his charts with unusual fidelity. He observed the great meteoric showers of 1866, 1872, and 1885, and collected together the different values for the positions of radiation, and obtained their mean places. It was from his averaged radiant for the November Leonids of 1866 that Professor Schiaparelli was successfully enabled to found his conclusions on the virtual identity of the orbits of this meteoric stream and Tempel's comet of 1866.

"An important paper by Professor Herschel appeared in the Monthly Notices for 1872, in which he called attention to certain showers presumably connected with Biela's periodical comet, and he pointed out the probability of a recurrence of the shower at the end of November, 1872, advising observers to maintain a watch of the sky at this particular period. His anticipations were realised in a very notable manner by the occurrence, on November 27, of one of the grandest meteoric exhibitions of modern times, which fully substantiated the theory of close association existing between comets and meteors, and certainly demonstrated that the slow meteors returning at intervals at the end of November really represented the *débris* of the lost comet of Biela.

"Valuable work was accomplished by Professor Herschel in the calculation of the radiant points of comets. A complete list of his results forming a valuable summary for reference and comparison was published in the 'British Association Report,' 1875, and in the same volume and also in Monthly Notices, vol. 38, p. 369, he gave lists of known accordances between cometary and observed meteor showers. In collaboration with Mr. R. P. Greg, he formed several catalogues of the radiant points of meteors observed by the British Association members, including one giving 88 positions in 1868, and another of 63 positions in 1875 (British Association Reports, 1868, 1872, 1875). Connected with the Luminous Meteor Committee of the British Association for many years and acting as Secretary, he drew up the

lengthy and valuable annual summaries of observations and general facts of meteoric progress which served more than any other cause to advance our knowledge of this branch of Astronomy during the period over which they extended, terminating in 1880. He also furnished the yearly Reports on the progress of Meteoric Astronomy for the Council of the R. Ast. Soc. until they were temporarily discontinued in 1881.

"Professor Herschel's writings were voluminous and marked by a precision and regard for detail which sufficiently showed his desire to omit nothing which could assist in forming correct deductions and serve as useful materials for study by future observers. His own practical work in this field of observation attained a high degree of excellence and others emulated the worthy example he had set. He often extended his watches for shooting stars into the morning hours and was unwearying in his efforts to observe not only the periodical showers, such as those of August and November, but equally endeavoured to trace out the more tenuous and exhausted streams of which the heavens furnish a multitude of examples. He encouraged and instructed other observers and stimulated them to take up work in the meteoric branch, offering, as he pointed out, the prospect of important and interesting discoveries.

"The value of a man's influence upon any branch of research cannot be fully judged from the results he himself accomplished. Professor Herschel by his prolific, agreeable and accurate writings led many others to interest themselves in recording meteors; and a pretty large proportion of the meteoric observations obtained during the last half century may be fairly said to have been initiated by the enthusiasm which he created and fostered in amateurs for this attractive branch of Astronomy."

But though the work on meteors engrossed the greater part of his scientific activity, Alexander Herschel had many other interests, as is testified by his numerous papers and bundles of correspondence. One of the chief of these was photography. His father was a keen and original photographer—the first man, it will be remembered, to use glass as a support for a photographic film (and the first picture he took in this way was of *his* father's great telescope). Alexander's devotion to photography was thus hereditary, and here, again, he not only worked assiduously himself but stimulated activity in others. The presentation of his portrait to the South Kensington Museum by the Amateur Photographic Association is recorded above, and among his treasured possessions was a beautiful album of photographs presented to him by the Newcastle-on-Tyne and Northern Counties Photographic Association (of which he was President, 1885—7) as a "slight acknowledgment of services rendered."

But his interests were wide and varied: plane waves, hedgehogs, astronomy, engineering; there is a large bundle of papers on fans for ventilation of mines, and another relating to a correspondence in 'Nature' with Professor P. G. Tait, in 1883, on the "Matter of Space." In 1900 he wrote for 'Nature' a long and careful review of the work of Piazzi Smyth in

spectroscopy. His brother, Colonel J. Herschel, has remarked on his extraordinary vitality; he nearly always *ran*, rather than walked, to his miscellaneous occupations and, however unexpectedly he might thus come across another member of the family, or an acquaintance, his alert mind prompted instantly some appropriate remark. But his mental activities had two unfortunate results: he shunned the interruptions of society so far as to become practically a recluse, taking all his meals alone, and he became impatient of his bodily needs until the neglect of them shattered his health. He died on June 18, 1907, at the age of 71, and on June 22 was buried in the grave at St. Laurence's Church at Upton, where his famous grandfather had been laid eighty-five years before.

H. H. T.

ADMIRAL SIR LEOPOLD MCCLINTOCK, K.C.B., F.R.S., 1819—1907.

WITH Sir Leopold McClintock we lose the chief leader and organizer of the Franklin searches. In experience of Arctic navigation and wintering he was second only to Sir James Ross. That great navigator was in the Arctic and Antarctic Regions during nineteen summers and eleven winters. McClintock experienced eleven navigable seasons and six winters. Parry, who comes next, had nine navigable seasons and four winters. Excepting some of Parry's companions, no other Arctic explorer approaches the record of these three, James Ross, McClintock, and Parry. As regards sledge travelling without the help of dogs, McClintock stands first, and will remain first, probably, for all time.

Francis Leopold McClintock was of a Scottish family, settled in Ulster in the early part of the seventeenth century, his father being the youngest son of John McClintock of Drumcar, co. Louth. His mother was the daughter of Dr. Fleury, then Archdeacon of Waterford, of an old Huguenot family from near Rochelle. The Archdeacon's wife was English. Leopold, the second son of a family of fourteen, was born at Dundalk on July 8, 1819. Through the interest of a cousin, who was first lieutenant of the "*Samarang*," a 28-gun frigate, young McClintock entered the navy before he had reached the age of twelve. During his seventeen years of sea service before entering upon his Arctic career, three things probably combined to stimulate his interest in a noble profession, and to form his character as a trustworthy officer and a thorough seaman. The first was his severe and arduous work in a surveying vessel in the Irish Sea. The second was his position as a junior commissioned officer when the paddle steamer "*Gorgon*," commanded by Captain Charles Hotham, was driven high and dry on the beach at Monte Video while

a furious *pampero* was blowing. The skill and ingenuity with which Captain Hotham succeeded, with the zealous co-operation of officers and men, in floating the vessel after several months, was looked upon as one of the finest feats of seamanship of the century. The details were described, in a book entitled "The Floating of the Gorgon," by Cooper Key, one of the lieutenants, who was eventually a Fellow of this Society. Soon afterwards the Commodore of the Station placed an acting lieutenancy at the disposal of Captain Hotham, and he at once gave it to young McClintock. This may be considered as a proof that the future Arctic explorer was amongst the most useful and zealous of those who were concerned in that famous and difficult feat in seamanship. The third event was McClintock's appointment as Third Lieutenant of H.M. brig "Frolic," in the Pacific. After a service of upwards of a year up the Gulf of California, McClintock became the First Lieutenant of the "Frolic," when he brought his knowledge, acquired under Sir Charles Hotham, to bear in raising a wreck in the Straits of Magellan. An English brig had been burnt and sunk in the anchorage of Punta Arenas. The officers and crew of the "Frolic" were employed for about three weeks in raising the vessel out of the anchorage, a difficult piece of work which was successfully performed. The wreck was placed on the beach, and specie to the value of £9000 was recovered. Her own crew had disappeared long before.

After the "Frolic" was paid off in June, 1847, McClintock went to study at the R.N. College at Portsmouth. Alarm was beginning to be felt at the long absence of Sir John Franklin's expedition, and two vessels, the "Enterprise" and "Investigator," were ordered to be fitted out under the command of Sir James Ross, to obtain tidings and bring relief. At that time Captain William Smyth, the second naval officer who ever descended the whole course of the River Amazon, was at the College, and was a friend of Sir James Ross. It was through Smyth's recommendation that McClintock was appointed Second Lieutenant of the "Enterprise." She was a sailing ship of 470 tons, with no auxiliary steam power. Sir James fully expected to meet his friends Franklin and Crozier in Barrow Strait, coming home. But it turned out far otherwise. It was a very close ice year, and Ross's vessels were obliged to winter in Port Leopold, at the N.E. end of North Somerset, having obtained no tidings of the missing expedition.

In the spring of 1849 Sir James Ross made a sledge journey of forty days, starting on May 15, which was then considered a sufficiently early date. He was accompanied by McClintock. He examined 500 miles of coast, most of it previously unknown, and his journey was the longest that had hitherto been made. But there were grave mistakes. The diet was quite insufficient, and the sufferings and privations were great. All the men were quite exhausted when they returned to the ship, and were laid up for weeks. The winter arrangements were defective, there was sickness and several deaths, and scurvy was in the ships when they returned to England in the autumn of 1849.

McClintock saw all the mistakes, and the way to avoid them in future. But the main result of his first Arctic voyage was his perception of the great future of sledge travelling. He saw that the work of the ship was to bring explorers to the threshold of their achievements, but that the actual discoveries must be made by sledges over the ice. He, therefore, devoted some months to a close study of the problems to be solved. The scale of diet must be improved, so as to keep the men strong and healthy, while the closest attention must be given to a reduction of the weights to be drawn. He also made experiments, with the assistance of Professor Samuel Haughton, on the best cooking apparatus, and on the rate of consumption of different kinds of fuel. The best clothing for Arctic sledging work also occupied his attention.

At this time McClintock had just reached his thirtieth year. With a short, lithe figure, and a well knit frame, he was well adapted for long-sustained endurance of hardships and fatigue. He had a genius for organisation, and was gifted with inventive faculty and a quick perception of the exact thing that was needed in an emergency. Though reticent, he took an interest in conversation, and was well informed. His manner was very quiet, but his firmness and resolution obtained for him the confidence and devotion of those who served under him. Always perfectly calm, he gave his orders in an emergency with decision, but without noise. He was a sympathetic friend and an excellent messmate.

The return of Sir James Ross without any tidings aroused the country. The "Enterprise" and "Investigator," with the "Plover," were sent to Bering Strait. Another expedition, commanded by Captain (afterwards Sir Horatio) Austin, was fitted out, to proceed by Baffin's Bay and Barrow Strait, consisting of two sailing vessels, the "Resolute" (Captain Austin), and the "Assistance" (Captain Ommanney), with two screw steam tenders, the "Pioneer" (Lieutenant Sherard Osborn), and the "Intrepid" (Lieutenant Cator). Two brigs, under Captain Penny, also went out to co-operate in the search.

McClintock was appointed First Lieutenant of the "Assistance," and the expedition left England in May, 1850. Captain Austin had served as a lieutenant with Sir Edward Parry in his third Arctic voyage. It was due to him that the ships under his command were perfectly well ventilated, dry, and comfortable. McClintock always gave Captain Austin the credit for the perfect winter arrangements, and for keeping the officers and men employed and amused. Austin certainly had a genius for detail, combined with warm sympathy and care for the welfare of those under his command. He was too old for sledge travelling, but for winter organisation he was unequalled.

But if McClintock justly gave this credit to Sir Horatio Austin, he himself was perfect as an Arctic First Lieutenant. The expedition was obliged to winter in the pack between Griffith and Cornwallis Islands, officers and men emerging from the long night in sound health, strong, cheerful, and full of zeal. This was due to McClintock as regards the "Assistance," which was the happiest and healthiest ship that ever wintered in the Arctic Regions.

Captain Austin wisely entrusted the arrangements for sledge travelling to McClintock. No record had been found at Franklin's first winter quarters at Beechey Island, and there was, consequently, no clue to indicate the direction the missing ships had taken. It was necessary to organise searches in every direction. This was possible, because there was assembled, in the spring of 1850, by far the largest body of men that ever acted together in the Arctic Regions, and probably ever will. No less than eight extended sledge parties were despatched in different directions, each with a *depôt* party, and every three with an auxiliary party. This great scheme was due to the genius of McClintock. He introduced the system of autumn travelling to lay out *depôts*, and of spring *depôt* and auxiliary parties to enable the extended parties to double their distances. He it was who planned the scale of diet best calculated to keep the men healthy and strong, and all the other arrangements for their comfort, while keeping the weights down to a minimum.

McClintock's own journey to Melville Island in 1851 covered the unprecedented distance of 800 miles. He was away eighty days from the ship, and his men came back in perfect health. It was a memorable triumph. All the other "Assistance" parties carried out their instructions and returned, having suffered nothing but from frost bites and snow blindness. It was a thoroughly well-conducted expedition. When the four vessels returned to Woolwich it was resolved by the Admiralty to send them out again. One division, consisting of the "Resolute" and "Intrepid," was to proceed to Melville Island, mainly with the object of relieving the "Investigator," some anxiety being felt owing to her long absence. This object was happily effected. The "Resolute" and "Intrepid" passed the winter of 1852—53 at Dealy Island, off the coast of Melville Island. McClintock did not fail to make provision for the winter amusements of the men. He felt its importance, although his temperament did not admit of his joining personally in anything but the actual arrangements.

In the severe autumn travelling of 1852, McClintock surpassed himself. He was away forty days, and laid out a *depôt* at a distance of 260 miles. His spring travelling in 1853 was the greatest achievement, with men alone, that has ever been done, and it remains unsurpassed. He started on April 4 and returned on July 13, being away 106 days, covering 1328 statute miles at a rate of 11 miles a day, and discovering 886 miles of new land, including the northern half of Prince Patrick Island.

The "Resolute" had a team of dogs, procured in Greenland, and they were found useful for keeping up communications. But for such a journey as McClintock made, and over such ground, British seamen are superior to dogs, and will always secure better and greater results. This memorable journey of 1853 proves the thorough efficiency of all McClintock's equipments, down to the minutest detail. He overlooked nothing.

The "Resolute" and "Intrepid" left Dealy Island in August, 1853, but were stopped by the ice in November, and forced to pass a second winter.

The officers and men did not return to England until the autumn of 1854. McClintock had been promoted to the rank of Commander on the return of Austin's expedition, and on his return in 1854 he received his rank of Captain.

His frequent applications failed to obtain for him the employment he had a right to expect during the Crimean War; but at last the crown of his Arctic labours was at hand. In 1857 news arrived that relics had been found amongst Eskimo, proving that the coast of King William Island was the direction that the search ought to have taken. The Royal Society took the lead in submitting a numerously-signed petition urging the Government to complete the search by sending a small and inexpensive expedition in that direction. The Government declined. Then Lady Franklin nobly came forward, and resolved to equip and despatch such an expedition at her own expense. She offered the command to McClintock, who promptly accepted, on April 18, 1857. The small steam yacht "Fox," of 177 tons, was bought and fitted out; the Admiralty supplying pemmican, ice gear, winter housings, chronometers, charts, and warm clothing. The President and Council of the Royal Society voted £50 for the supply of magnetic and other instruments. Besides McClintock, the officers were Lieutenant Hobson, who had served in the "Plover," Captain (now Sir Allen) Young, of the Mercantile Marine, who contributed £500 towards the expenses, and the surgeon, Dr. David Walker. The crew consisted of twenty-four souls, of whom seventeen had already served in the Arctic Regions.

The "Fox" was unfortunately caught in the Melville Bay ice, and forced to pass the winter drifting down Baffin's Bay and Davis Strait. In the spring she broke out during a gale of wind, with huge masses of ice plunging about and crashing against each other in a heavy sea. The ship was for some time in extreme peril. But instead of seeking a port for rest and refreshment, McClintock calmly turned the head of his little vessel once more Northward Ho! Taking his old friend Carl Petersen on board in Greenland, with a team of dogs, he reached Beechey Island and erected Lady Franklin's memorial to her husband and his companions. He then made his way down Prince Regent's Inlet, and wintered in a bay, which he named Port Kennedy, on the north side of Bellot Strait.

By his famous spring journey round King William Island, McClintock obtained many relics from the Eskimo as well as statements. He found that the Franklin Expedition had discovered the continuance of sea between the Atlantic and Pacific; he collected a great number of memorials and relics; and by finding the record at Point Victory, he discovered the fate of Franklin.

Hobson had previously been over the ground on the north shore, and Allen Young made an important discovery along the southern coasts of Prince of Wales Island. The engines of the "Fox" had been partly taken to pieces for the winter. The engineer died, and the two stokers knew nothing about the engine. It is another instance of McClintock's mechanical knowledge and

skill that, with his own hands, he put the engine together and got it into working order.

On the return of the "Fox" in September, 1859, McClintock's reception was most cordial. The Admiralty ordered that his time in the "Fox" was to count as service in a man-of-war. He received the honour of Knighthood, honorary degrees of Oxford, Cambridge, and Dublin, the Freedom of the City of London, and of the Grocers' Company.

His modest but excellent narrative of the voyage of the "Fox" went through several editions, and the last one of 1882 has been stereotyped.

McClintock's next service was again in the Arctic Regions, and it was a most arduous one. He received command of the "Bulldog," a paddle-wheel steamer, wholly unadapted for service in the ice. He was to carry a line of deep-sea soundings from the Faroë Islands to Iceland, Greenland, and Labrador. Furious gales were encountered and, after tremendous work among the ice, with paddles bent and floats smashed, the "Bulldog" reached Godthaab in Greenland. The difficult task was eventually completed, and the "Bulldog" returned safely, though she was more than once in danger, needing the calmness, presence of mind, and consummate seamanship of such a man as McClintock for her safe navigation. Dr. Wallich was the naturalist of the "Bulldog." This scientific voyage completed McClintock's Arctic work, and in 1865 he was elected a Fellow of the Royal Society.

Sir Leopold's Arctic services had for their objects the relief of his missing countrymen, and, later, the discovery of their fate. He worked in the cause of humanity. Still, he never lost sight of the interests of science, and missed no opportunity of furthering them whenever he was able to do so. His extensive geographical discoveries did not consist of land merely seen from a ship, but of coasts traversed on foot and closely examined. His collection of miocene fossils from Atanakerdluk, obtained from the Inspector of North Greenland, was a valuable addition to Professor Heer's enumeration of the forest plants of the miocene age in that region. He enabled Professor Haughton to prepare the geological map and memoir of the Parry Archipelago, and the note on tidal streams, which form appendices to the voyage of the "Fox." And the North West Passage! The discovery of a continuous sea from the Atlantic to the Pacific by Franklin, by McClure, by Murray Parkes, was not the discovery of a *passage*. On the contrary, Professor Haughton has explained the reasons why a *passage* by any of those routes is impossible. With this knowledge, McClintock pointed out that the only *passage* is by the channel between King William Island and Boothia; and that, in a favourable year, there is no difficulty in passing through it. Sir Allen Young attempted it in a bad ice year in 1875, and the gallant Norwegian seaman, Amundsen, has completed the passage quite recently. McClintock, by the light of Professor Haughton's note on tidal streams, first pointed out the only possible North West Passage. Sir Leopold's last service to science, before his election as a Fellow of this Society, was his command of the "Bulldog."

He continued to serve his country afloat for many years. He had the "Doris" frigate in the Mediterranean, the "Aurora" in the West Indies, and was next appointed to the "Aboukir," as Commodore, at Jamaica. Returning home in 1869 he stopped for Drogheda at the request of the Carlton Club, but was unsuccessful. Soon after becoming a Rear Admiral, he was appointed Admiral Superintendent of Portsmouth Dockyard from 1872 to 1877, where he fitted out the Arctic Expedition of 1875. Sir Leopold was next Commander-in-Chief on the North American and West Indian station from 1879 to 1883. On his return he was elected an Elder Brother of the Trinity House, and continued to be an active member of that important Corporation for many years. In 1890 he was created a Knight Commander of the Bath.

In 1870 Sir Leopold had married Elizabeth Annette, daughter of Mr. Dunlop, of Monasterboice House, and of a daughter of Viscount Ferrand and Viscountess Massereene in her own right. He leaves a widow and five children, three sons and two daughters.

Sir Leopold McClintock continued to work, so far as the increasing infirmities of old age would admit, until the end of his long and useful life, which took place after he had reached the age of eighty-eight. He died on November 21, 1907. The illustrious explorer has left a name which is revered and honoured in every civilized country, and his loss will long be mourned alike by his surviving old shipmates and by many newer friends and admirers.

C. R. M.

HENRI MOISSAN, 1852—1907.

HENRI MOISSAN was born in Paris, on September 28, 1852. His father was a native of Toulouse; his mother, whose maiden name was Mitelle, was of an Orleans family. Moissan's features and his bright vivacious manner betrayed his southern origin; he was of the best French type.

His education, after school life, began in the Collège de Meaux; and in his twentieth year he entered the laboratory of Frémy at the Musée d'Histoire Naturelle, attending at the same time the lectures of Henri Sainte-Claire Deville, and Debray. He made good progress and, after spending a year at elementary work, he removed to the neighbouring laboratory of Decaisne and Dehérain, in the École Pratique des Hautes Études, with whom he worked on chemical problems bearing on vegetable life. While there, he passed the examinations required for graduation, taking the preliminary degree of Bachelier in 1874; of Licencié in 1877; in 1879 he became "Pharmacien de première Classe"; and in 1880 he qualified as "Docteur ès Sciences physiques."

After working with Dehérain for little more than a year, he left the Museum to direct a small laboratory of his own; and he then abandoned the study of vegetable chemistry for that of inorganic chemistry, a branch to which he remained faithful for the rest of his life, and in which he achieved the highest distinction. This private laboratory was given up somewhat later; and he then found quarters with MM. Debray and Troost, in the laboratories of the Sorbonne.

In 1879, he was appointed "Répétiteur de Physique" at the Agronomic Institute; and after spending a year in that position, he was promoted to the post of "Maître de Conférences" and "Chef des Travaux Pratiques," or lecture assistant and senior demonstrator at the École Supérieure de Pharmacie, a position which he held till 1883. A year before this change, he had been appointed, after a competitive examination, "Agrége des Sciences physiques-chimiques," and his standing among his fellows at that date was such that on the death of Professor Bouis, in 1886, he was elected to the Professorship of Toxicology in the School of Pharmacy; he retained that chair till 1899, when his turn came in rotation to occupy the chair of "Mineral" or Inorganic Chemistry; he then for the first time delivered a course of lectures on that branch of Chemistry.

In 1900 he was appointed Assessor to the Director of the School; and in the same year, on the death of Professor Troost, the Professor of Inorganic Chemistry in the Faculté des Sciences in the University of Paris, Moissan was unanimously chosen as his successor, for his name had become very widely known owing to his remarkable discoveries. At the same time he retained the title of Honorary Professor at his old school, the École de Pharmacie.

Moissan's first research was conducted in conjunction with Dehérain; it had reference to the interchange of oxygen and carbon dioxide in the leaves of plants which had been exposed to the subdued light of a darkened room.

His first work in the domain of inorganic chemistry dealt with the oxides of the iron group of metals, and especially with compounds of chromium. His thesis for the doctorate contained an account of a portion of this research. In it he described the existence of two allotropic modifications of chromium sesquioxide: one obtained by igniting ammonium chromate, as well as by other methods, insoluble in acids, unattacked by hydrogen sulphide and by oxygen; the other, produced by careful drying of the hydrated oxide at 440° , which, when heated to 140° in a current of hydrogen sulphide, gave a black Cr_2S_3 , reducible to CrS by further heating in a current of hydrogen. Oxygen converted this variety of sesquioxide into the analogue of manganese dioxide, CrO_2 , a dark grey powder.

This train of thought led Moissan to investigate the products of reduction of the oxides of the iron group. The so-called "pyrophoric iron," obtained by heating ferrous oxalate, was shown to consist of ferrous oxide, FeO ; the same substance is produced by reducing the sesquioxide, Fe_2O_3 , in a current of a mixture of carbon dioxide and hydrogen. The action of hydrogen at 330° to 440° reduces Fe_2O_3 to Fe_3O_4 , and the magnetic oxide is also formed by heating the sesquioxide in a current of carbon monoxide at the temperature of melting zinc. It is only at 500° to 600° that ferrous oxide is produced; it is pyrophoric at ordinary temperatures. But pyrophoric iron itself can be obtained by heating the sesquioxide for a long time in a current of perfectly dry hydrogen to 440° , or by distilling away the mercury from an amalgam of iron.

An allotropic variety of magnetic oxide, Fe_3O_4 , was produced by heating the monoxide, or metallic iron reduced by hydrogen, to redness in a current of moist hydrogen. It formed a black magnetic powder, incandescing and changing to Fe_2O_3 when heated in air. At 1500° , Fe_2O_3 gave off oxygen, and was converted into a very resisting modification of the magnetic oxide.

Somewhat similar researches were carried out on the oxides of manganese, nickel, and cobalt, and pyrophoric varieties of the metals were prepared.

Having obtained metallic chromium from its amalgam, Moissan next investigated the little-known chromous salts, preparing pure chromous chloride, CrCl_2 ; also the blue sulphate, $\text{CrSO}_4 \cdot 7\text{H}_2\text{O}$, which is amorphous with copperas; chromous acetate, chromous bromide, and chromous oxalate. The acetate or the chloride, on treatment with a solution of potassium cyanide, gave the interesting compound $\text{K}_4\text{CrC}_6\text{N}_6$, analogous to yellow prussiate of potash, oxidisable to the red $\text{K}_3\text{CrC}_6\text{N}_6$. A final paper on the blue compound of CrO_3 with peroxide of hydrogen, in which it was shown that the ratio between the two is $\text{CrO}_3 : \text{H}_2\text{O}_2$, ends the series.

In 1884, Moissan turned his attention to the investigation of compounds of fluorine. He prepared phosphorous fluoride first, by heating copper phosphide with lead fluoride. It is a gas, exploding when sparked with oxygen, and yielding POF_3 . He next prepared fluoride of arsenic, by distilling a mixture

of arsenious oxide, sulphuric acid, and calcium fluoride. He electrolysed this liquid, and produced from it elementary arsenic, and a gas which attacked the platinum electrode. On submitting phosphorous fluoride to a rain of sparks, phosphorus was deposited; the product, however, was not fluorine, but PF_5 , the liberated fluorine combining with the phosphorous fluoride. These researches occupied him until 1888. In that year he investigated some organic fluorides, obtaining $\text{C}_2\text{H}_5\text{F}$ by the interaction of ethyl iodide and silver fluoride, and the corresponding methyl and isobutyl fluorides. In the following year he made the capital discovery that while the compound $\text{KF} \cdot 2\text{HF}$ melts at 65° , $\text{KF} \cdot 3\text{HF}$ remains liquid at -23° , and conducts electricity electrolytically. And this long series of researches culminated in the discovery of elementary fluorine.

During this work he accumulated useful information, which enabled him to adapt his apparatus to the end he had in view. One method which he attempted for the isolation of fluorine was to pass phosphorous and phosphoric fluorides over red-hot platinum sponge. A gas was evolved, which liberated iodine from a solution of potassium iodide; but this gas came off very slowly, and was absorbed largely by the platinum tube in which the experiment was made. He next tried the electrolysis of arsenious fluoride; but he found that that liquid is a very poor conductor, and he attempted to increase its conductivity by the addition of anhydrous hydrofluoric acid; better results, however, were obtained on addition of anhydrous potassium fluoride to the mixture of arsenious fluoride and hydrofluoric acid; and from this it was but a step to omit the arsenious fluoride and to electrolyse the mixture of acid and potassium salt.

His first apparatus was made of platinum; the electrodes were rods of platinum-iridium alloy, thickened at the ends, so as to last longer; for the negative electrode was always rapidly corroded. Paraffined corks closed the ends of his first platinum U-tube. The cork closing the limb into which the negative electrode passed was corroded and charred; hence, in his next experiment, corks were replaced by flourspar stoppers, cemented into hollow platinum cases on which a screw was turned, so that the stoppers could be screwed tight into the two open ends of the U-tube. This experiment was successful in yielding fluorine; while hydrogen came off from the positive electrode, and passed out through a side branch of platinum tube, fluorine was evolved at the negative pole; it passed out through a similar platinum tube, and was made to play on various materials, exposed to its action in a platinum capsule.

It was found that sulphur, selenium, and tellurium inflamed, giving white deposits; the first combines, as Moissan subsequently found, to form a gas, SF_6 . From phosphorus, PF_3 and PF_5 were obtained; iodine caught fire and burned; Moissan subsequently found that IF_5 was the product; bromine lost its colour, and again Moissan and his pupils proved this to be due to the formation of BrF_3 ; on pure carbon at ordinary temperature fluorine had no action; but both boron and silicon caught fire and burned, giving SiF_4 and BF_3 .

By blocking the exit of either of the tubes conveying away the hydrogen or the fluorine, one or other gas could be caused to pass round the bend and mix; when a bubble passed round, a detonation occurred, showing that hydrogen and fluorine combine even in the dark at the low temperature of -35° , for the apparatus had to be maintained at this low temperature to prevent the admixture of gaseous hydrofluoric acid with the fluorine. The low temperature was conveniently attained by surrounding the U-tube with liquid methyl chloride.

Most metals were instantly attacked, some with inflammation; even platinum and gold could not resist its action; but they had to be raised to 400° before action took place. Salts such as potassium iodide, mercuric iodide, and lead iodide were completely decomposed, giving fluorides both of the metal and of the iodine. Chlorine was liberated from potassium chlorate, along with oxygen, on which fluorine had no action; chlorine was also evolved from carbon tetrachloride, the tetrafluoride being formed; and water was instantly decomposed, its oxygen being liberated as ozone.

Although all these properties of this gas could be most easily explained on the assumption that it consisted of fluorine, still they might conceivably appertain to a mixture of ozone and hydrofluoric acid, or to a perfluoride of hydrogen, HF_n . The former supposition was disproved by trying the action of such a mixture; but none of the properties of the gas were manifested. The second hypothesis was also disproved by leading the fluorine over iron and proving that no hydrogen passed on.

Subsequent research showed that the formation of fluorine was not so simple as had at first been supposed. Investigation of a muddy deposit, which was always found at the bend of the U-tube on dismantling it, showed that that substance consisted mainly of the compound K_2PtF_6 ; and that in all probability it was the substance undergoing electrolysis; the equivalent of the potassium being liberated at the cathode as hydrogen, and fluorine at the anode, the group PtF_4 again combining with potassium fluoride. The operation did not proceed with regularity until a considerable quantity of platinum had dissolved from the anode.

The density of the gas was found to be 18.3, on the hydrogen standard. But this figure, which is too low, was almost certainly due to the presence of oxygen, produced by the electrolysis of water still dissolved in the electrolytic mixture. Moissan for long supposed that, on passing the current, the water accidentally present first underwent electrolysis, before the fluorine appeared; but it was subsequently found that water still remained to be electrolysed, even after much fluorine had been separated. Later experiments, in which the gases other than fluorine were estimated in the gaseous mixture weighed, and allowance was made for their presence, proved that the true density of fluorine is 19, a figure identical with the atomic weight. The supposition that fluorine consisted partly of monatomic molecules mixed with an excess of diatomic molecules had therefore to be abandoned. The activity of fluorine was not to be explained by its monatomicity.

The reason why fluorine cannot be produced by heating PtF_4 , tetrafluoride of platinum, was found as soon as that substance was prepared by the action of fluorine on platinum; it is because that compound decomposes water, and therefore cannot be prepared in the wet way.

Moissan also attempted to induce combination between argon and helium and fluorine, but without success, even when the mixture was submitted to discharge of powerful sparks.

The preparation of two gaseous fluorides of carbon led Moissan to attempt to remove the fluorine, in the hope that the carbon would be liberated in the form of diamond. But this hope was disappointed; the product was always lamp-black. The experiments led to the discovery of the method of preparing the diamond artificially; it had been found that a meteorite from Cañon Diablo, consisting, as meteorites usually do, mainly of metallic iron, had imbedded in it small crystals of diamond; and Moissan's genius led him to divine the cause of their formation; his theory was that the carbon had originally been dissolved in the iron, when it was in a molten state; that the surface of the iron had suddenly cooled; and that the iron in the interior, on solidifying, was subjected to great pressure; for solid iron containing carbon in solution occupies a larger volume than molten iron. These considerations directed his experiments, which were crowned with success.

His first experiments, in which the iron was saturated with carbon at about 1000° , were, however, not successful; he accordingly argued that at higher temperatures the solubility of carbon in iron should increase, as is the general rule; and he devised the electric furnace to attain much higher temperatures. His three great investigations are seen thus to hang together; one suggested the other, and Moissan's skill and patience brought them all to a successful conclusion. The spirit in which he carried out his work is well expressed in his own words, which occur in the preface to his book on the "Electric Furnace":—"But what I cannot convey in the following pages is the keen pleasure which I have experienced in the pursuit of these discoveries. To plough a new furrow; to have full scope to follow my own inclination; to see on all sides new subjects of study bursting upon me; that awakens a true joy which only those can experience who have themselves tasted the delights of research."

Moissan's electric furnace, designed not for technical but purely for experimental work was of the simplest construction. It consisted of a rectangular block of lime, made of the excellent Paris limestone, in the centre of which a hole had been scooped. This block was covered with a rectangular lid; two grooves of circular section admitted the carbon poles which served as electrodes, and an arc was made between the poles. Later, an electromagnet was used to deflect the arc downwards, so that it might play more directly on the object to be heated. A current of 100 to 125 ampères, at 50 or 60 volts, was employed in his earlier researches.

The volatilisation of the material of the crucible, lime, was the first fact to be chronicled. Indeed, two torrents of what appeared to be flame poured

out through the holes admitting the electrodes. These apparent flames were, however, only white-hot lime dust, condensed from the lime-vapour which filled the furnace. Subsequently, to save cost, the body of the furnace was constructed of limestone. The crucible to be heated stood on magnesia, to avoid the rapid formation of calcium carbide; and, for some purposes, crucibles were constructed of a grid of alternate slices of carbon and magnesia. By heating an inclined carbon tube in the arc, and feeding in at one end a mixture of an oxide such as chromium oxide and carbon, the metal flowed out at the other end, and a continuous supply was thus obtainable.

The temperature of such electric furnaces appeared to depend on the quantity and intensity of the current; but it is limited, no doubt, by the temperature of volatilisation of carbon.

By help of this powerful engine of research, Moissan succeeded in causing many changes to occur, and in producing many compounds previously unknown. Some of these compounds have had important commercial applications; others are of great interest, owing to the reactions which they undergo, and the light that they shed on the problems of chemical combination.

Among the products of the electric furnace were:—Crystallised lime, strontia, baryta, and magnesia; distilled copper, silver, platinum, tin, gold, iron, and uranium; volatilised carbon and silicon, and many other similar products. Carbides of the metals of definite composition and properties were often formed; thus from aluminium, Al_4C_3 was obtained in yellow crystals, giving pure methane on treatment with water; in many cases excess of carbon crystallised out in the form of graphite as the metal cooled.

In his systematic search for a method to produce artificial diamonds, Moissan investigated numerous varieties of graphite; he subjected varieties of carbon to the intense heat of the electric furnace, in order to study their behaviour and, as before remarked, he studied the Cañon Diablo meteorite, in which small diamonds are imbedded. These researches made him familiar with the behaviour of carbon under all possible circumstances, and enabled him to separate diamonds from other materials with which they might be mixed.

The first actual experiment of crystallising carbon under pressure from iron was made with 200 grammes of Swedish iron, fused in the electric furnace for six minutes with sugar charcoal in a carbon crucible. The crucible was then seized with tongs and plunged into a vessel full of cold water. Moissan relates the anxiety with which this was first attempted; an explosion was feared; but, although the water boiled, no accident occurred then, nor, indeed, during some hundreds of similar experiments. The iron was dissolved in dilute hydrochloric acid; the residue, chiefly consisting of carbon in various forms, was extracted with nitro-hydrochloric acid, and alternately with boiling sulphuric and hydrofluoric acids. It was then, in order to remove graphite, boiled with nitric acid and potassium chlorate. The final residue was "floated" in bromoform, in which some transparent

dust, of density 3 to 3.5, sank, while a black substance floated. The transparent particles scratched ruby, burned to carbon dioxide, and showed octahedral facets.

Among the products of the electric furnace in Moissan's hands must be mentioned metallic chromium, manganese, molybdenum, tungsten, uranium, vanadium, zirconium, and titanium; and carbides of lithium, calcium, barium, strontium, cerium, lanthanum, yttrium, thorium, aluminium, manganese, and uranium. Moissan studied the action of water and acids on these new compounds, and determined the proportions of hydrogen and hydrocarbons which they yielded. He also prepared silicides of iron, of chromium, and "carborundum," now the trade name for carbide of silicon; as well as borides of iron, carbon, and the metals of the alkaline earths.

These researches were described in two works, '*Le Fluor*,' published in 1887, and '*Le Four Électrique*,' published ten years later. Since that date, Moissan's chief researches are as follows:—The preparation of calcium by heating calcium iodide with sodium; its success depends on the easy attack of sodium by alcohol, while calcium is hardly affected; sodium ammoniums and methyl ammoniums, obtained by the action of sodium on liquid ammonia and on methylamine; similar bodies obtained from lithium and calcium; the hydrides of calcium, sodium, and potassium, in a memoir concerning which he shows that these bodies are non-conductors of electricity, and that the hydrogen must be considered to be a non-metal; in later papers he describes a most ingenious formation of sodium formate by the action of carbon dioxide on sodium hydride; and of sodium hyposulphite, $\text{Na}_2\text{S}_2\text{O}_4$, by treating the hydride with sulphur dioxide.

Moissan did not, however, desert his old favourites, fluorine and the products of the electric furnace; for in later years he prepared thionyl fluoride, SOF_2 , and sulphuryl fluoride, SO_2F_2 , both gases; and he redetermined the density of fluorine in a dry glass vessel. The electric furnace yielded him metallic niobium and tantalum; many metals of the rare earths; and borides of silicon. A silicide of lithium, Li_6Si_2 , was prepared; and a new hydride of silicon, Si_2H_6 , the analogue of ethane. He also studied the acetylides of metals of the alkalis. His last research, of which an account appeared in the '*Comptes Rendus*' for 1906, p. 675, dealt with the distillation of titanium in the electric furnace. In all, he published more than 300 memoirs and notices.

This incomplete account of Moissan's work shows how productive his laboratory was; he was full of new ideas, most of them offshoots of his original great discoveries; much of his work was carried out in conjunction with students, of whom an increasing number came from abroad; for his reputation both as a skilled chemist and as an attractive personality had become world wide. His work lay almost entirely in the field of inorganic chemistry; and it contributed to turn the tide which had set so long in favour of organic research.

He published, along with many other collaborators, a treatise on inorganic

chemistry—"Traité de Chimie Minérale"—in five large volumes, which has already a large circulation in France, and in point of detail is a very complete account of inorganic compounds.

Moissan was the recipient of numerous honours, not only in his own country, but also abroad. In 1888, after his isolation of fluorine, he was elected a member of the Académie de Médecine; in 1891, of the Académie des Sciences; in 1895, membre of the Conseil d'Hygiène de la Seine; and in 1898, of the Comité Consultatif des Arts et Manufactures. He was foreign member of the Royal Society of London; an honorary member of the Royal Institution and of the Academies of Denmark, Vienna, Belgium, Upsala, Haarlem, Amsterdam, New York, and Turin, besides numerous others. He was also Commandeur de la Légion d'Honneur.

In 1887 the Institut awarded him the Prix Lacaze, one of its most valuable gifts; he was the Davy medallist in 1896, and the Hofmann medallist in 1903; and he obtained honours from the Franklin Institute of Philadelphia, from the Société d'Encouragement pour l'Industrie Nationale, and the Société Industrielle du Nord de la France. And in 1906, shortly before his death, he was awarded the Nobel Prize for Chemistry.

Moissan was a practised speaker, and a perfect expositor. His lectures at the Sorbonne were crowded by enthusiastic students, all eager to catch every word; and he kept their attention for an hour and three quarters at a time, by a clear, lucid exposition, copiously illustrated by well-devised experiments. His command of language was admirable: it was French at its best; the charm of his personality and his evident joy in exposition gave keen pleasure to his auditors. He will live long in the memories of all who were privileged to know him, as a man full of human kindness, of tact, and of true love of the subject which he adorned by his life and work. Perhaps the key to his character lies in his own words:—"Nous devons tous placer notre idéal assez haut pour ne pouvoir jamais l'atteindre"; or, as our own poet has put it:—"O but a man's reach should exceed his grasp; or what's a heaven for?"

W. R.

WILLIAM HENRY PERKIN, 1838—1907.

SIR WILLIAM HENRY PERKIN, whose death occurred on July 14, 1907, was born in London on March 12, 1838. He was the youngest son of Mr. George Fowler Perkin, a builder and contractor, who died in 1865 at the age of 63. The younger Perkin received his early education at a private school, and was afterwards sent to the City of London School, where it may be said that his inborn talent for chemistry as a science first took definite form through the encouragement of the late Thomas Hall, who was at that time one of the class masters in the school. Science at that period apparently did not form a recognised part of the educational curriculum, since Mr. Hall had to take the time for giving two weekly lectures on chemistry and natural philosophy out of the dinner interval. The schoolboy Perkin attended these lectures with the greatest delight, often sacrificing the midday meal in his enthusiasm, and was soon promoted to the, to him, proud position of being allowed to prepare the experiments, and help Mr. Hall with the demonstrations during the lectures.

It is evident that in the case of Perkin, as is so generally the case with those who leave their mark upon any branch of science, the particular specialisation of faculty and disposition indicative of inherent ability revealed itself at a comparatively early age, and it is certainly a fortunate circumstance that at this critical period of his career he should have fallen under the influence of Mr. Hall, who was himself a pupil of Hofmann's, and who, according to all accounts furnished by contemporaries, must have been highly inspiring as a teacher of science. Perkin has quite recently placed upon record the history of his early life in the following passage:—

“As long as I can remember, the kind of pursuit I should follow during my life was a subject that occupied my thoughts very much. My father being a builder, the first idea was that I should follow in his footsteps, and I used to watch the carpenters at work, and also tried my hand at carpentering myself. Other things I noticed led me to take an interest in mechanics and engineering, and I used to pore over an old book called ‘The Artisan,’ which referred to these subjects and also described some of the steam engines then in use, and I tried to make an engine myself and got as far as making the patterns for casting, but I was unable to go any farther for want of appliances. I had always been fond of drawing, and sometimes copied plans for my father, whose ambition was that I might be an architect. This led me on to painting, and made me think I should like to be an artist, and I worked away at oil painting for some time. All these subjects I pursued earnestly and not as amusements, and the information I obtained, though very elementary, was of much value to me afterwards. But when I was between twelve and thirteen years of age, a young friend showed me some chemical experiments, and the wonderful power of substances to crystallise in definite forms, and

the latter, especially, struck me very much, with the result that I saw there was in chemistry something far beyond the other pursuits with which I had previously been occupied. The possibility also of making new discoveries impressed me very much. My choice was fixed, and I determined if possible to become a chemist, and I immediately commenced to accumulate bottles of chemicals and make experiments."

It was at this period that Perkin entered the City of London School, and, as he has told us in the passage just quoted, with a distinct bias towards chemistry as a career. This decision appears to have caused his father some disappointment, as at that time chemistry as a profession offered but few attractions, and it was only through the intercession of Mr. Hall that he was allowed, at the age of fifteen, to enter the Royal College of Chemistry as a student under Hofmann in the year 1853. His special ability must have revealed itself also to the eminent professor who was at the head of that institution, for he soon passed through the ordinary course of training, consisting of qualitative and quantitative analysis and gas analysis, and, by the end of his second year, had, under Hofmann's guidance, carried out his first piece of research work. In describing this period of his career in a speech delivered in New York in October, 1906, Perkin significantly added with respect to the ordinary curriculum which all students of the Royal College of Chemistry went through at that time:—"This I looked upon only as a preliminary part of my chemical acquirements and not, as many used to and some still do, as a full equipment. Research was my ambition . . ."

For a youth with these proclivities, no more inspiring influence existed in this country than that exercised by Hofmann in the research laboratory in Oxford Street, and at the age of seventeen we find Perkin, who had by then proved his capabilities, enrolled as honorary assistant to the Professor. In that laboratory the first serious insight into research methods was acquired, and it is of particular interest to note that his initiatory work, instigated by Hofmann, was in connection with the hydrocarbon anthracene, a substance which, a few years later, served as the starting point in one of the most brilliant synthetical achievements in scientific and industrial chemistry, with which the name of Perkin will be always associated. No less interesting is the circumstance that this first research, although, for reasons which are now readily intelligible, ending in negative results, in no way daunted the ardour of the young investigator, who, in later life, frequently declared that his first efforts at getting definite products from anthracene were of invaluable service to him when he again took up the study of this hydrocarbon from the scientific and technical point of view. The problem set by Hofmann was, in fact, not solved until more than a quarter of a century after Perkin's first attempt, and then by a very indirect method. The general subject which, among others, was under investigation in the Oxford Street laboratory at that time was the production of organic bases from hydrocarbons by the reduction of the nitro-derivatives. Anthracene, then known as "paranaphthalene," had not been brought within the range of these experiments, and the task of

isolating the hydrocarbon from coal-tar pitch with a view to nitrating the pure substance was entrusted to Perkin, whose difficulties in attempting on a laboratory scale to achieve a result which is only satisfactorily accomplished on a factory scale are readily imaginable. However, the aid of the tar distiller was invoked, and a supply of the raw anthracene obtained from the Bethels Tar Works, but the pure hydrocarbon could not be nitrated, and so the desired amine corresponding to aniline could not be obtained. As a matter of fact, Perkin had unwittingly produced, by the action of nitric acid upon anthracene, the parent substance of alizarin, anthraquinone, although his analyses failed to reveal the nature of the compound, because at that time an erroneous formula had been assigned to the hydrocarbon by its discoverers, Dumas and Laurent. Other (haloid) derivatives of anthracene prepared during the research for a similar reason failed to give intelligible results on analysis, and the young investigator was therefore given another piece of work, viz., the study of the action of cyanogen chloride upon naphthylamine, this being a part of a general research upon the action of cyanogen chloride, etc., upon organic bases, which had, for some time, been going on under the auspices of Hofmann. This second investigation was brought to a successful issue and communicated a year later to the Chemical Society of London, which then held its meetings at a house in Cavendish Square.

Perkin's first successful research was thus completed in 1855 and appeared in the *Journal of the Chemical Society* in 1856 (vol. 9, p. 8; also Liebig's 'Annalen,' vol. 98, p. 238) from which time, throughout the whole period of his career, that Society received and published practically the whole results of his scientific labours.

The compound described by Perkin in his first paper as "menaphthylamine," in accordance with the nomenclature of the period, is the α -dinaphthylguanidine of modern chemistry. But one naphthylamine was known at that time, and the possible existence of a second modification could not, in the existing state of chemical theory, have been foreseen. That the work and the worker found favour in the estimation of Hofmann is shown by the circumstance that on its completion he was promoted from the position of honorary assistant and made a member of the research staff, his colleague being Mr., now Professor, Arthur Herbert Church, with whom Perkin formed a friendship which lasted throughout his life. It was at this period of his career that he made that discovery of the dyestuff mauve, which for a time diverted his attention from pure to applied science, although, as is now well known, the cause of pure science was advanced at a later period by this discovery to an extraordinary degree, and in many directions quite unforeseen at the time. The story of the discovery of the first coal-tar colouring matter has been frequently placed upon record, and the fiftieth anniversary was made the occasion for an international celebration in London, in July, 1906, when Perkin became the central figure and received the homage and congratulations of chemists and technologists from every part of the world. Seldom, if ever, in the history of science has the discovery of one chemical

compound of practical utility led to results of such enormous scientific and industrial importance as this accidental preparation of mauve in 1856. The details of the working out of the manufacturing process and of the methods for utilising the dyestuff belong to the history of applied science, but since the discovery was the outcome of purely scientific antecedents, and its achievement a matter which materially affected Perkin's career, it is necessary to recapitulate this chapter of his activity in the present notice.

The remarkable zeal which Hofmann's young assistant must have thrown into his work is well revealed by the circumstance that even the activity of the Oxford Street laboratory failed to satisfy his craving for research. He was at that time kept at work upon the investigations prompted by that illustrious professor whose resourcefulness appeared to be inexhaustible, and had little or no time for working independently. He accordingly fitted up, in 1854, a part of a room as a laboratory in his own home,* and there carried on his researches after the day's work at the College was over and during the vacation. It is of considerable interest to note that even at this early period his work brought him into contact with colouring matters, for, having secured the co-operation of his colleague, Mr. Church, one of the first pieces of work which they took in hand was the investigation of the products of reduction of dinitrobenzene and dinitronaphthalene. From the latter there was obtained a coloured substance which, in accordance with the prevailing views concerning the nature of such compounds, was named "nitrosonaphtylene," and a brief account of it was given to the Royal Society by Hofmann on February 6, 1856,† the complete description being afterwards published in the names of Perkin and Church in the Journal of the Chemical Society.‡ The interest attaching to this colouring matter is that it was the first representative of the large and important group of azo-dyes derived from naphthalene ever manufactured, although its true nature was, of course, at first unknown to its discoverers, and even its ultimate composition was not accurately established at the time, because, seven years later, when Perkin and Church resumed the study of the compound, they found that it contained no oxygen, as had at first been supposed, and that it could be made more conveniently by the action of a nitrite upon a salt of α -naphthylamine in the presence of alkali. The substance was renamed, in accordance with current notions, "azodinaphthyl-diamine," and the amended results published by the Chemical Society.§ A patent was also secured (No. 893 of 1863)|| and the substance had a limited use as a dyestuff. The azodinaphthyl-diamine of 1863 is the α -aminoazonaphthalene of modern chemistry, and, it may be added, is of no importance in tinctorial industry at the present time.

* His father's house was at that time known as "King David's Fort," Shadwell, E. The name is still preserved in King David's Lane.

† 'Roy. Soc. Proc.,' vol. 8, p. 48.

‡ 'Quart. Journ.,' 1857, vol. 9, p. 6.

§ 'Chem. Soc. Journ.,' 1863, vol. 16, p. 207.

|| It has been pointed out by Caro ('Berichte,' 1891, vol. 24, Appendix, p. 3) that this patent is the first claiming the production of a sulphonated azo-colour.

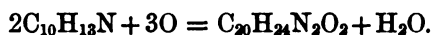
The discovery of a compound which happened to be a colouring matter was at this stage of Perkin's career an accidental circumstance,* as was, in fact, the discovery of mauve, which was made in this same rough home laboratory about the same time, viz., the Easter vacation of 1856. In view of the widespread notion that discoveries of industrial value are invariably the result of researches directed solely towards this practical end, it may be of interest to place once again upon record the statement that the first coal-tar colouring matter was discovered by Perkin as the outcome of as distinct a piece of pure scientific research as was possible in the light of the theoretical conceptions of that period. It must be borne in mind that in 1856 organic chemists had practically nothing to guide them in expressing the formulæ of compounds but the ultimate composition derived from analytical results. It is true that the possibility of different substances having the same ultimate composition had, since the time of Wöhler and Berzelius, received recognition among chemists, but these early ideas concerning isomerism had not yet given birth to those definite conceptions of chemical structure which at a later period resulted from the application of the doctrine of valency. Thus in 1856 it was scientifically legitimate to set out from the assumption that a natural product might be synthesised if the elements composing it could be brought into combination in the right proportions. Many attempts to produce natural compounds artificially had been made on this principle since the fundamental synthesis of urea from ammonium cyanate by Wöhler in 1828, and although no success in the way of the desired syntheses can be recorded, there can be no doubt that many indirect results of lasting importance to chemical science were arrived at in this way. The discovery of mauve by Perkin is an example of such an indirect result which at first ranked as an industrial success only, and, it may now be said fortunately, for a time diverted the energies of its discoverer from the field of pure science to that of chemical industry.

In so far as the discovery of mauve is attributable to scientific as distinguished from purely technical research, it may be pointed out that in accordance with the prevailing belief that a synthetical product, if of the same empirical formula, would prove to be identical with the natural compound, Hofmann, as far back as 1849 had, as Perkin himself indicates in the Memorial Lecture,* suggested the possibility of synthesising quinine from naphthalene, the ground for this suggestion being that the base "naphthalidine" (= naphthylamine) was at that time supposed to differ from quinine only by the elements of two "equivalents" of water, so that if the hydration of the base could by some means have been effected, quinine might be expected to be the result.† Ideas of this order were prevalent in the chemical world about the middle of the nineteenth century, and Perkin has told us how, imbued with these notions, he was "ambitious enough to wish to work on this

* 'Chem. Soc. Trans.,' 1896, vol. 69, p. 603.

† 'Reports of the Royal College of Chemistry,' 1849, Introduction, p. 61.

subject of the artificial formation of natural compounds.”* Following the method then in vogue, he came to the conclusion that the most likely generator of quinine would be allyltoluidine, since two “equivalents” of this compound, by taking up oxygen and losing hydrogen (in the form of water), would give a substance of the formula of quinine—



The experiment was tried, a salt of allyltoluidine being oxidised by potassium dichromate, but, instead of quinine, a “dirty reddish-brown precipitate” was obtained. This result, negative in one sense, still appeared of sufficient interest to the young investigator to be worth following up, and he repeated the experiment with a salt of the simpler base aniline, obtaining in this case a very dark-coloured precipitate, which, on further examination, was found to be a colouring matter possessed of dyeing properties. Thus was discovered the first of the coal-tar dyes, the subsequent and rapid development of which, from a laboratory curiosity into a technical product, brings into strong prominence the extraordinary combination of energy, skill, and resourcefulness inherent in this youth, who at the time was not much over seventeen years of age. The very fact of his continuing the investigation of what the majority of contemporary chemists would have discarded as an unpromising “Schmier,” may be taken as an indication of his originality, for it must be remembered that, at that time, the main object of research in organic chemistry was to obtain definite crystalline compounds, and the formation of non-crystalline, and especially of coloured, amorphous products, was considered as an indication of the failure of a reaction. This view of research method was particularly upheld in Hofmann’s laboratory, and, as has frequently been pointed out by many critics of the too-rigid enforcement of this method, there can be no doubt that the discovery of the coal-tar dyes was considerably retarded by the liberal use of animal charcoal as a decolourising material. Hofmann himself, for example, is well known to have prepared rosaniline in 1858 incidentally as a by-product in the course of his study of the reaction between carbon tetrachloride and aniline, although, so far as concerned the main objects of his research, he regarded it as an impurity. To Perkin must be given the credit of having the courage to break through the traditional dislike of investigating coloured, resinous-looking products, an achievement which, in the case of mauve, may, perhaps, be attributed to that rare combination of the scientific and artistic faculties which he was known to possess. The fact that his new product on purification gave a compound which, at that time, would be considered as imparting a beautiful shade of colour to fabrics when used as a dye, may fairly be claimed to have appealed to his æsthetic sense, and to have lured him on with his research, independently, at first, of immediate practical developments. Professor A. H. Church, his colleague and co-worker, has supplied the following statement with respect to this period of his career:—

* Hofmann Memorial Lecture, *loc. cit.*

"It was, I think, in October, 1853, that William Henry Perkin entered the Royal College of Chemistry, and was assigned the next bench to mine in the front of the building, looking out upon the street. One year before this date I had gone through my novitiate, and had been awarded what was called a scholarship—still receiving instruction and attending the lectures, but paying no fees. Indeed, I had been carrying out from time to time some minor researches suggested by Dr. Hofmann. Perkin and I soon found we had several interests in common. We were both given to painting, and were amateur sketchers. I was introduced to his home at King David's Fort, and we began painting a picture together. This must have been soon after the Royal Academy Exhibition of 1854, when I had a picture hung. I was nearly four years Perkin's senior, but was soon impressed by his mental activity and his devotion to work.

"I remember the epoch-making experiment in which mauve was first discovered. He repeated it in my presence for my particular benefit. I distinctly recollect strongly urging him to patent his invention. Shortly after this date I left the college for Oxford, but Perkin and I were in frequent communication, and sometimes worked together after I had taken my degree in 1860, and until my appointment in 1863 to the chair of chemistry at the Royal Agricultural College.

"During the year 1855, and the spring of 1856, Perkin and I were no longer working in the same laboratory, for I had been given a bench in the professor's private laboratory on the ground floor, and was engaged in carrying out some of his most important researches of that period."

The history of the technical development of this discovery has been narrated by Perkin in his Hofmann Memorial Lecture of 1896, and it is only necessary to go through that account in order to realise the magnitude of his achievement. A youth of about eighteen, undaunted by the discouragement of his professor, the greatest living master of organic chemistry, had determined to work out his discovery on a manufacturing scale, with no experience or training as a manufacturer himself, and with no precedent to guide him in the construction of plant for carrying on operations, which had, up to that time, never been conducted on more than a laboratory scale. Hofmann's opposition to his young assistant's leaving the paths of pure science, and embarking upon what, no doubt, appeared to his maturer judgment a most risky undertaking, is quite understandable, and fully justifiable. Everything in connection with the new industry had to be worked out from the very beginning—the methods for the isolation and preparation of the raw materials, as well as the manufacture of the new dyestuff, and the prejudices of the dyers and printers against innovation had also to be overcome. With all this responsibility ahead of him, Perkin, encouraged, no doubt, by the favourable report concerning the dyeing qualities of his new product furnished by certain practical dyers, and especially by Messrs. Pullar, of Perth, formally resigned his position at the Royal College of Chemistry, and boldly entered upon his career as an industrial chemist. He

has touchingly placed upon record his indebtedness to his father, who, although, as already stated, at first inclined to be adverse to his taking to chemistry as an occupation, had, at the time of the discovery of mauve, so much confidence in his son's ability that he threw in his lot with the new venture, and devoted the greater part of his life's savings to the building of a factory, for which a site had been secured at Greenford Green, near Sudbury, at which latter place Perkin afterwards resided. His elder brother,* Thomas D. Perkin, who, during the summer vacation of 1856, had assisted in making mauve in the laboratory on a somewhat larger scale, in order to supply specimens for testing by the dyers, also joined in the undertaking. A patent was secured (No. 1984, August 26, 1856), and the building of the works commenced in June, 1857, and six months later the new dyestuff, under the name of "Aniline Purple," or "Tyrian Purple," was being manufactured in sufficient quantity to supply one of the London silk dyers.† The subsequent development of this precursor of the coal-tar dyes forms an interesting and, indeed, a romantic chapter in the history of applied science. Its reputation spread rapidly; from silk dyeing its application was extended to cotton dyeing and to calico printing, and at every stage of a career, which may be fairly described as triumphant, the master hand of William Henry Perkin can be detected. Now we find him working out processes for the manufacture of nitrobenzene and aniline on a scale never before attempted, then we learn of his introducing improvements into the methods of silk dyeing on the large scale, and of his discovering suitable mordants for enabling the dyestuff to be applied to cotton fibre both by dyers and calico printers. Well may it be said in Perkin's own words: "In fact, it was all pioneering work."‡

In spite of these splendid pioneering efforts, however, it seems that the recognition of the value of the product at first took place but slowly in this country, and it was not until it had been taken up in France that its merits for tinctorial purposes became generally recognised. In a private communication addressed to the writer of this notice on April 3rd, 1906, Perkin states:—"The value of the mauve was first realised in France, in 1859. English and Scotch calico printers did not show any interest in it until it appeared in French patterns, although some of them had printed cloth for me with that colour." The "Société Industrielle de Mulhouse," it may be added, awarded him a silver medal for his discovery in 1859, and afterwards a gold medal.§ It is of interest to note also that a paper was read by him at the Leeds Meeting of the British Association, in 1858, under the title:

* Born 1831, died 1891.

† The name "Mauve," by which it was afterwards generally known, was given to the dyestuff in France.

‡ Speech at the Jubilee Banquet in New York, October 6, 1906. See also the Hofmann Memorial Lecture, *loc. cit.*, p. 609.

§ The impetus given to the new colouring matter through French influence was also referred to by Perkin in his reply to Professor Haller at the Jubilee Meeting in 1906: (Report, p. 11); see also 'Journ. Society of Dyers and Colourists,' April, 1907, p. 106.

"On the Purple Dye obtained from Coal Tar" (Reports, 1858, p. 58), when specimens of the substance and fabrics coloured by it were exhibited. No more appropriate place than this town, in the centre of one of the chief seats of the tinctorial industry in Great Britain, could possibly have been selected for bringing the discovery under the notice of chemists and technologists. Sir John Herschel was President of the Chemical Section, and by a remarkable coincidence, in the opening address of the President of the Association, Professor (afterwards Sir Richard) Owen, there occur the following passages *à propos* of the general progress of organic chemical synthesis:—"To the power which mankind may ultimately exercise through the light of synthesis, who may presume to set limits? Already, natural processes can be more economically replaced by artificial ones in the formation of a few organic compounds It is impossible to foresee the extent to which chemistry may ultimately, in the production of things needful, supersede the present vital agencies of nature." This pronouncement at the Meeting when the first of the coal-tar colouring matters was exhibited—a discovery which laid the foundations of an industry which now supplies as tar products the colouring matters of madder and indigo—may be looked upon as prophetic.

With the increase in the demand for the new colouring matter, the Greenford Green factory had to be enlarged, and at one period the quantity of mauve required by the dyers and printers was more than could be supplied by the working plant in use. An archil dye of a somewhat similar shade, made in France, was introduced into this country under the name of "French Purple," and used as a substitute for mauve, pending the execution of the orders received at Greenford Green. The scale of manufacture of the raw material had necessarily to be also increased, and it appears that the resources of the Greenford factory were so taxed that the aid of another firm of chemical manufacturers had to be secured in order to prepare nitrobenzene. This firm, Simpson, Maule, and Nicholson, had an establishment at Locksfields, in the south of London, and their connection with the early history of the new industry is of interest, for the reason that at a later period they also took up the manufacture of coal-tar colouring matters, Mr. Edward Chambers Nicholson, who had, about a decade before the discovery of mauve, been among Hofmann's most brilliant pupils, having during his connection with this branch of manufacture made many discoveries of the greatest importance. In calling attention, however, to the rapid growth of the coal-tar colour industry, it may be necessary to insert a caution in order to prevent an exaggerated idea of the scale of operations being formed by those who are unacquainted with the details of the early stages. The production of the raw materials and of the finished product was large only in comparison with the laboratory operations conducted in glass flasks, beakers, and retorts. But even when transferred to the factory, the operations were carried on at first on what would now be considered only an experimental scale with very primitive appliances, so enormously has the

size and perfection of the plant in this branch of manufacture been increased since the foundations were laid by Perkin in 1856.*

The influence of this inaugural work by Perkin upon the subsequent history of the industry is too well known to need recapitulation. It is only necessary to point out that the introduction of aniline—at that time a mixture of homologues—into the market soon led other investigators to enter the field of colour chemistry, and new dyestuffs made their appearance in rapid succession, the most noteworthy after mauve being magenta, which was discovered as a technical product in 1859, by Verguin, and manufactured for a short period by his process† by the firm of Renard Frères et Franc, of Lyons. In fact, the stream of competition in the course of a few years turned against the original mauve, the demand for which gradually fell off as other colouring matters of a similar or brighter hue were introduced. The consideration of chief interest in connection with Perkin's successful venture into the domain of applied chemistry is, however, from the present point of view, the influence which his work in this field exerted upon pure science. That it has exerted an enormous influence is now generally recognised, and a critical examination of the course of development of the industry will show that the gain by chemical science has been of a twofold character—a direct and an indirect gain.

In the first place, as the direct result of introducing into commerce in large quantities organic chemical products which had before been but laboratory curiosities, a great stimulus was given to research, and chemical workers of the highest repute took up the investigation of the new products, both raw materials and colouring matters. As an indirect consequence, also, many new compounds of industrial value were discovered incidentally in the course of manufacturing operations conducted on the large scale, and these, with the colouring matters which from time to time appeared as novelties, furnished endless subject matter for research, the results so obtained often proving of the greatest scientific importance. Not the least interesting circumstance in connection with this chapter of chemical history is the fact that Hofmann himself soon entered the field of tinctorial chemistry, to which he made many contributions of the utmost value both from the scientific and technological point of view. He was, in fact, for many years recognised as the leading scientific authority on coal-tar colouring matters, and

* The manufacture of nitrobenzene was at first carried on in large glass flasks or "boltheads" and it was even impossible in the early days to get nitric acid of sufficient strength to nitrate the benzene, so that a mixture of sulphuric acid and sodium nitrate had to be used. It was afterwards found that cast-iron vessels could be employed, and the scale of production was thus considerably increased. It may be of interest to place upon record that there still survives at an advanced age one of the men, William Underwood, who was employed in the early manufacture of nitrobenzene at the works in Locksfields in 1856, and who remembers the development of the operation from "bolt-heads" to iron stills. This information has been furnished to the writer by Dr. W. Fleming, of Pirbright, who knows and has attended the man.

† By heating crude aniline (*i.e.*, aniline containing toluidine) with stannic chloride.

many of his discoveries were practically utilised in the factories. Then, again, there can be no doubt that the success of the new industry and the succession of important scientific discoveries which followed its development attracted large numbers of students into the chemical schools, and many gifted and active workers were by this means drawn as recruits into the ranks of scientific chemists. It is, indeed, not going too far to say that the discovery of the coal-tar colouring matters brought about such a revival in the study of organic chemistry, and particularly in that of the so-called "aromatic" series, that when the epoch-making conception concerning the constitution of these compounds had been given to the world by Kekulé in 1865, the rapid extension of the "benzene theory" was enormously facilitated by the resources which the new industry had given to pure science. If it is true that the new theory materially advanced the cause of the industry, it is no less true that the industry contributed to the advancement of the theory, the verification of which might have been delayed for a generation or more without such support. No better illustration of the interdependence of science and industry has ever been given to the world than this particular example of the action and reaction between theoretical and applied chemistry.*

The success of the new industry not only reacted upon the science of chemistry in the way indicated, but it may be claimed that, contrary to Hofmann's forebodings, it proved in the long run beneficial in every way to Perkin himself, and through him to that science to which he devoted his life. He has told us that when, being fully convinced of the value of mauve, he announced his intention of leaving the College of Chemistry and taking up the manufacture of the new colouring matter, he determined not to allow the manufacturing career to check his research work, and nobly did he adhere to his resolution. His published papers show that in spite of all his technical work the stream of original investigation was never allowed to stagnate. Only a year after the starting of the Greenford works, viz., in 1858, in conjunction with Duppa, he discovered that aminoacetic acid or "glycocoll," a compound which up to that time had only been prepared by the decomposition of natural products, could be obtained by heating bromoacetic acid with ammonia.† A general survey of his work during his

* The consideration of the later important influence upon other branches of science arising, often in most indirect and unforeseen ways, from the applications of coal-tar products to such subjects as bacteriology, histology, therapeutics, photography, etc., would swell this notice to an inordinate extent. Although results of incalculable value have been achieved in these fields, Perkin himself is not particularly identified with any of the lateral developments of his initial pioneering labours. References to this aspect of the subject were made in some detail at the Jubilee celebration in 1906. (See the official Report published by the Memorial Committee, and also a paper by Dr. Hugo Schweitzer in 'Science,' No. 616, October 19, 1906, p. 481.)

† Perkin and Duppa, 'Liebig's Annalen,' vol. 108, p. 112. This discovery is specially referred to, not only as illustrating Perkin's extraordinary activity during this busy period, but also because the compound is the type of a large group of amino-acids which of late years have become of extreme importance owing to their relationship to the proteins, as shown by Emil Fischer and his co-workers.

connection with the coal-tar colour industry, which ceased in 1874, brings out very clearly the double line of thought which during that period actuated his research work. Concurrently with the investigation of the dyestuffs, he carried on researches in other departments of organic chemistry which had at that time no relations with tinctorial chemistry. Thus we find that by 1860 he, in conjunction with Duppa, had discovered the relationship between tartaric and fumaric-maleic acid, and had effected the synthesis of racemic acid from dibromosuccinic acid, a line of work which was followed up with signal success.* About 1867 he must have commenced those researches on the action of acetic anhydride upon aromatic aldehydes which led to such important developments and culminated in that beautiful method of synthesising unsaturated acids now known as the "Perkin synthesis." The first paper of this series bore the title "On the Action of Acetic Anhydride upon the Hydrides of Salicyl, Ethylsalicyl, etc.,"† and as the outcome of this work the synthesis of coumarin, the odorous substance contained in Tonka Bean, etc., was announced the following year.‡ The production of a vegetable perfume from a coal-tar product was thus first made possible by Perkin, and the continuation of this work, after his retirement from the industry, led to his celebrated discovery of the synthesis of cinnamic acid from benzoic aldehyde, an achievement which subsequently, in the hands of Adolf v. Baeyer and H. Caro, made possible the first synthesis of indigo from tar products.§ It is of interest to note also that while still in the coal-tar colour industry he took part in the discovery of synthetical methods for producing glyoxylic acid from dibromacetic and bromoglycollic acids, thus giving the first insight into the constitution of glyoxylic acid, a result of considerable significance in view of the important part attributed by many modern chemists to this acid in the photosynthetic processes going on in growing plants.||

The research work done during Perkin's colour-making period was carried on in a laboratory in a house just outside the Greenford factory, where also the scientific investigations in connection with the colouring matters were conducted, the double line of work already indicated being revealed by the papers published during that period. It has not been considered necessary to give a complete list of these papers in the present notice, but it will be of

* Perkin and Duppa, 'Liebig's Annalen,' 1860, vol. 115, p. 105; 'Chem. Soc. Journ.,' 1860, vol. 13, p. 102; Perkin, 'Chem. Soc. Journ.,' 1863, vol. 16, p. 198; Perkin and Duppa, 'Liebig's Annalen,' 1864, vol. 129, p. 373; Perkin, 'Chem. Soc. Proc.,' 1888, vol. 4, p. 75.

† 'Chem. Soc. Journ.,' 1867, vol. 20, p. 586.

‡ "On the Artificial Production of Coumarin and Formation of its Homologues," 'Chem. Soc. Journ.,' 1868, vol. 21, pp. 53 and 181.

§ "A Preliminary Notice of the Formation of Coumarin, Cinnamic Acid, and other similar Acids," 'Chem. News,' 1875, vol. 32, p. 258; "On the Formation of Coumarin and of Cinnamic and of other Analogous Acids from the Aromatic Aldehydes," 'Chem. Soc. Trans.,' 1877, vol. 31, p. 388.

|| Perkin and Duppa, 'Chem. Soc. Journ.,' 1868, vol. 21, p. 197.

interest to call attention to the fact that the purely scientific study of the colouring matters undertaken at this time centred round his early discoveries. It was in this new laboratory at Greenford that he and Church continued the investigation of "azodinaphthyldiamine" already mentioned, and discovered a method for resolving this compound by complete reduction, thus introducing a process which is still the standard one for determining the constitution of azo-compounds, and at the same time leading to the isolation of the first diamine derived from naphthylamine.* Nor did he allow his scientific interest in his first discovered dyestuff to flag, for one paper on mauve from the purely chemical point of view was published during his connection with the industry and another after his retirement in 1874.†

In 1868 it was shown by Graebe and Liebermann that the colouring matter of the madder, alizarin, one of the most ancient of vegetable dyestuffs and a substance of immense value for tinctorial purposes, was a derivative of the coal-tar hydrocarbon anthracene, and not, as had up to that time been believed, a derivative of naphthalene. The synthesis of this compound was effected by Graebe and Liebermann in that year, and patents for its manufacture from anthracene secured in Germany and in Great Britain, this being the first instance of a natural vegetable colouring matter having been produced artificially by a purely chemical method. This discovery had a great influence upon Perkin's career as an industrial chemist, and may, indeed, be considered to have marked a new phase of his activity in this field. There was no living worker in this country at that time besides Perkin who so completely combined in himself all the necessary qualifications for taking advantage of such a discovery. Imbued with the spirit of his early ambition to produce natural compounds synthetically, with more than a decade's experience as a manufacturer, with the resources of a factory at his disposal, and, not least, with special experience of anthracene as the very substance upon which, at Hofmann's instigation, he commenced his career in research work, it can readily be understood that Graebe and Liebermann's results should have appealed to him with special significance. The first patented process of the German discoverers was confessedly too costly to hold out much hope of successful competition with the madder plant, requiring as it did the use of bromine. Perkin at once realised the importance of cheapening the process by dispensing with the use of bromine, and undertook researches with this object. As a result, the following year (1869) witnessed the introduction of two new methods for the manufacture of artificial alizarin. In one of these processes dichloranthracene was the starting point, and in the other the sulphonic acid of anthraquinone, the first

* 'Chem. Soc. Journ.,' 1865, vol. 18, p. 173.

† "On Mauve or Aniline Purple," 'Roy. Soc. Proc.,' 1863, vol. 12, p. 713 (abstract); 1864, vol. 13, p. 170 (full paper). "On Mauveine and Allied Colouring Matters," 'Chem. Soc. Trans.,' 1879, vol. 35, p. 717. In 1861 he lectured before the Chemical Society on the new coal-tar colouring matters, on which occasion, he has told us, Faraday was among his auditors and congratulated him at the end of the lecture.

being of special value in this country owing to the difficulty of obtaining at that time "fuming" sulphuric acid in large quantities. The second process, which is the one still in use, had quite independently been worked out in Germany by Caro, Graebe, and Liebermann, and patented in England practically simultaneously with Perkin's.* The subsequent industrial development of this brilliant achievement has now become historical; the artificial alizarin has completely displaced the natural colouring matter, and madder growing as an industry has become extinct. It is of interest, as showing the growth of the new industry, to reproduce Perkin's statement in 1876:—

"The quantity of madder grown in all the madder-growing countries of the world, prior to 1868, was estimated to be 70,000 tons per annum, and at the present time the artificial colour is manufactured to an extent equivalent to 50,000 tons, or more than two-thirds of the quantity grown when its cultivation had reached its highest point."†

The development of this branch of the coal-tar industry in the Greenford Green Factory has also been recorded by Perkin:—

"Before the end of the year (1869) we had produced 1 ton of this colouring matter in the form of paste; in 1870, 40 tons; and in 1871, 220 tons, and so on in increasing quantities year by year . . . up to the end of 1870 the Greenford Green Works were the only ones producing artificial alizarin. German manufacturers then began to make it, first in small and then in increasing quantities, but until the end of 1873 there was scarcely any competition with our colouring matter in this country."‡

This brilliant achievement in technology again served to bring out the purely scientific spirit which animated all Perkin's work. The chemical investigation of anthracene derivatives was carried on concurrently with the industrial development of the factory process, and also after his retirement, about a dozen papers on these compounds having been published between 1869 and 1880. The discovery of a practical process for the manufacture of alizarin thus led to the utilisation of another coal-tar hydrocarbon anthracene, which had up to that time been a waste product, and the methods for isolating and purifying this substance had, as in the case of benzene, etc., to be worked out in the factory. All the difficulties inseparable from large-scale operations with new materials were successfully surmounted by Perkin; the increasing demand for artificial alizarin taxed all the resources of the factory, and by 1873, when the necessity for introducing enlarged plant became imperative, advantage was taken of the opportunity for transferring the works to the firm of Brooke, Simpson, and Spiller, the successors to the firm of Simpson, Maule, and Nicholson, which had co-operated with Perkin in the early days of the mauve manufacture.

* The patents are, Caro, Graebe, and Liebermann, No. 1936, of June 25, 1869, and W. H. Perkin, No. 1948, of June 26, 1869.

† Presidential Address to Section B of the British Association, Glasgow, 1876, 'Reports,' p. 61.

‡ Hofmann Memorial Lecture, 'Chem. Soc. Trans.,' 1896, vol. 69, p. 632.

The present "British Alizarine Company" afterwards took over the works from Brooke, Simpson, and Spiller, and removed the manufacture from Greenford Green to Silvertown, so that the latter factory is the lineal descendant of the original establishment which gave the first coal-tar colouring matter to tinctorial industry.

On completion of the sale of the Greenford Green Works in 1874, Perkin retired after eighteen years' connection with the industry. In view of the enormous development of this branch of manufacture in later times, it is of interest to recall the circumstance already mentioned that the whole output of the original factory, both in number and quantity of products, would appear quite trivial in comparison with that of one of the great German factories now in existence—a fact which only serves to emphasise the extraordinary fertility of the seed originally planted by Perkin, whose labours as a technologist led, as a practical issue, to the acquisition of sufficient means to enable him to withdraw altogether from the industrial side of chemistry at the comparatively early age of 36, while still in the prime of life. By many who have watched the decadence of the coal-tar colour industry in this country, he has been blamed for cutting himself so soon adrift from his own offspring. There is no doubt that the life of the industry here would have been prolonged if he had kept in touch with it, but it must not be forgotten that at the time of his retirement he left things in a very flourishing condition. Other factories had developed into successful establishments, and Great Britain was well to the front in this

branch of manufacture. Neither Perkin nor his contemporaries could have foreseen in 1874 that our position would later be so successfully assailed by foreign competitors. To a man with his most moderate personal requirements, and with the ardour of the original investigator unquenched, the means of retirement—modest enough as compared with the fortunes accumulated by modern successful manufacturers—simply meant the opportunity of giving practical effect to that resolution concerning his mission as a research chemist which he had formed as a youth, which he had adhered to throughout his industrial career, and which it was his desire to carry out untrammelled by business distractions throughout the remainder of his working period.* Industry may, and, no doubt, did, lose by his decision, but science gained by thirty years of his activity from the period of his retirement down, practically, to the end of his life.

The contributions to chemical science which proceeded from Perkin's laboratory after 1874 have, to some extent, been referred to. After his connection with the Greenford Green Factory had terminated, he had a new house built at Sudbury, converting the adjacent house in which he had previously resided into a laboratory, and it was here that from 1875 he continued his investigations of those colouring matters with which his

* "The great importance of original research has been one of the things I have been advocating from the commencement of my chemical career, in season and out of season."
—From a speech by Perkin at the Jubilee Banquet in London, on July 26, 1906.

manufacturing experience had brought him into contact, such as mauveïne, the anthracene derivatives, etc. In 1881 he first drew attention to a certain physical property of some of the compounds which he had prepared, viz., their magnetic rotary power, which observation diverted his activity into an entirely new channel. On further development in his hands this method became a powerful weapon in dealing with questions of chemical constitutions, and the remainder of his life was more or less devoted to its elaboration. As Perkin's name must always be intimately associated with this chapter of physical chemistry, it will be of interest to place upon record his earliest observation. In a paper entitled "On the Isomeric Acids obtained from Coumarin and the Ethers of Hydride of Salicyl"* he describes the methyl ether of " α -methylorthoxyphenylacrylic acid," which he had first prepared in 1877, and in this paper occurs the statement:—

"A determination of its magnetic rotary power gave for the yellow ray 2.334, water being taken as 1. Test observations were made at the same time with water and carbon bisulphide, and gave results very nearly identical with those obtained by Becquerel."†

It is not difficult to follow, at least conjecturally, the mental process by which Perkin was enabled to foresee that this property might be utilised for investigating the constitution or structure of chemical molecules, a subject which even at that time was beginning to bristle with difficulties and ambiguous results when handled by purely chemical methods. He had for precedent the success which had attended the study of other optical properties of organic compounds, such as ordinary (not induced) rotary power, dispersion, refractivity, etc., and he threw himself seriously into this line of work, armed with the skill of an accomplished experimenter, and with that true instinct as a chemist which enabled him to deal with his materials in such a manner that his results at once commanded complete confidence, in spite of the circumstance that this kind of work was for him a totally new departure. In 1882 he published a preliminary paper on the application of this method, and a complete account in 1884.‡

From that time onwards the Chemical Society received and published constant instalments of his work, the fertility of the method being shown not only by the long list of papers published in his own name, but also by the numerous observations recorded in the papers of other workers, to whose service his apparatus and his observational powers were frequently and ungrudgingly devoted. His achievements in this field are well summarised in a letter from Professor J. W. Brühl, of Heidelberg, himself one of the

* 'Chem. Soc. Trans.,' 1881, vol. 39, p. 409.

† 'Ann. Chim.,' 1877 (5), vol. 12, p. 22. *Loc. cit.*, p. 411.

‡ "On Rotary Polarisation by Chemical Substances under Magnetic Influence," 'Chem. Soc. Trans.,' 1882, vol. 41, p. 330. "On the Magnetic Rotary Polarisation of Compounds in Relation to their Chemical Constitution; with Observations on the Preparation and Relative Densities of the Bodies examined," *ibid.*, 1884, vol. 45, p. 421. This last paper, which occupies 60 pages of the volume, contains a full description of the apparatus and method of observation.

pioneers in the application of optical methods for the determination of chemical constitution, sent to the writer of this notice for transmission to Perkin on the occasion of the Jubilee celebration in 1906: "Availing yourself of the marvellous discovery of your great countryman, Michael Faraday, you undertook to investigate the relations between the chemical composition of bodies and their magnetic circular polarisation—that is to say, one of the general properties of all matter. Before you began work there was little, almost nothing, known of this subject, certainly nothing of practical use to the chemist. You created a new branch of science, taught us how, from the magnetic rotation, conclusions can be drawn as to the chemical structure of bodies, and showed that the magnetic rotation allows us to draw comprehensive and certain conclusions as to the chemical constitution of substances, just as we may from another general physical property, viz., refraction and dispersion. And by showing that both these physical methods of investigation lead to completely harmonious results, you did essential service to both the branches of study, and also to chemistry, which they are destined to serve."

This last statement by Brühl, which relates to one of the most interesting results of the study of magnetic rotation, has reference to a development of Perkin's work, which brought him into association with the late John Hall Gladstone, the pioneer and leading authority in this country at that time on the relations between refractive and dispersive power and chemical constitution. The correspondence between the results arrived at by these two optical methods forms the subject of a joint paper by Gladstone and Perkin published in 1889.* Eighteen years later, Perkin's last paper, to which attaches the melancholy interest that it was read before the Chemical Society on April 18, 1907, only a few months before his death, bears the title: "The Magnetic Rotation of Hexatriene, $\text{CH}_2:\text{CH}:\text{CH}:\text{CH}:\text{CH}_2$, and its Relationship to Benzene and other Aromatic Compounds: also its Refractive Power."†

Although, as already stated, the latter part of Perkin's life was devoted mainly to his work on magnetic rotation, he published also during this period a few papers relating to other subjects, among which perhaps the most notable is his contribution to the subject of low temperature combustion, entitled "Some Observations on the Luminous Incomplete Combustion of

* "On the Correspondence between the Magnetic Rotation and the Refraction and Dispersion of Light by Compounds containing Nitrogen," 'Chem. Soc. Trans.,' 1889, vol. 55, p. 750. The correspondence between Perkin and Gladstone during this period has been placed at the disposal of the writer by Miss Gladstone. The letters are interesting as showing the extreme conscientiousness in every detail with which Perkin carried out his work. The results are embodied in the above paper, and a further contribution by Perkin was published two years later, under the title, "The Refractive Power of certain Organic Compounds at different Temperatures," 'Chem. Soc. Proc.,' 1891, vol. 7, p. 115. In his later papers he dealt with refractivity as well as magnetic rotation ('Chem. Soc. Trans.,' 1896, vol. 69, p. 1; *ibid.*, 1900, vol. 77, p. 267, etc.).

† 'Chem. Soc. Trans.,' 1907, vol. 91, p. 806.

Ether and other Organic Bodies.”* The writer of this notice well remembers the keen interest with which the experiments were followed in the darkened meeting room of the Chemical Society at Burlington House when this paper was read. In view of the modern revival in the scientific study of the chemical mechanism of combustion, it is of importance that Perkin's observations should not be allowed to fall into oblivion.

It has been claimed in a previous part of this notice that Perkin's entry into the domain of chemical industry was no real loss, but actually a gain to pure science. His published papers, considered in detail, show that his contributions to “colour chemistry” are far outweighed by his work in other fields. In fact, the extension and completion of the investigation of the dyestuffs of his industrial period is due to other workers, and Perkin's achievements in this direction are, on the whole, more of a technological than of an abstract scientific character, the constitution of most of the colouring matters having been subsequently worked out chiefly by the group of brilliant continental investigators attracted by the success of the new industry, and stimulated by the rapid development in chemical theory then going on in Germany.† But although Perkin has over-shadowed his own achievements as a “colour chemist” by his subsequent career, the whole success of his life, and the inestimable gain which chemical science has derived from his labours, must be directly attributed to his industrial undertakings, for it may safely be asserted that had he not been rendered independent by the success of the Greenford Green Factory, he would never have found an opportunity for that continuous devotion to research which is so essential for the achievement of results of lasting value. Having determined in early life to adopt chemistry as a career, he would of necessity have been compelled to become either a manufacturer or to have entered an educational establishment. In the former capacity he would, no doubt, have succeeded, but in any subordinate post he might have spent long years before acquiring independence. As a teacher his prospects of making a position at the time of his connection with the Royal College of Chemistry were most slender. There were but very few posts which he could have filled; originality as an investigator was of minor importance as a qualification for the teaching profession, and the stamp of university training was generally considered absolutely essential for holding any important appointment in that profession. Perkin in any minor teaching post would have been lost to science. Happily the comparatively rapid financial success of his early discoveries placed him in that category which comprises such names as Cavendish, Herschel, Joule, Murchison, Spottiswoode, Lyell, and Darwin—representatives of that band of independent

* ‘Chem. Soc. Trans.’ 1882, vol. 41, p. 363.

† For example, the constitution of mauveine was established broadly by O. Fischer and Hepp about 1880; that of the colouring matters of the rosaniline group (magenta, methyl violet, etc.), by E. and O. Fischer, about 1878, and that of safranine about 1883 by Nietzki.

devotees of science who have more than any other class helped to maintain the prestige of this country. Truly may it be said that to a man of his temperament success as a manufacturer meant salvation as an original worker.

Reviewing Perkin's scientific work as a whole, its chief characteristic is its solidity. His mind was not of that order which readily entered into the region of speculation; he was a typical representative of that school of chemists to whom the conscientious accuracy of experimental facts is of primary importance—the school which has laid those solid foundations of chemical science upon which all superstructures of theory must be erected. It is for this reason that it may be predicted with certainty that his work will live in the history of modern chemistry whatever changes in theoretical conceptions the future may have in store. He himself witnessed with the progress of the science radical changes in the views of chemists concerning the mechanism of the reactions or the nature of the compounds which he had discovered. With true philosophic spirit he accepted the evidence of other workers and welcomed the legitimate development of his own discoveries. Whatever modification of theory may have been rendered necessary by the accumulated labours of the great and ever-growing army of investigators which he lived to see following the tracks which he had been the first to tread, it may safely be asserted that his own early footprints have been, and always will be, ineffaceable.

Perkin was by disposition a man of extreme modesty and of a most retiring nature. His devotion to science and the domesticity of his character accounted so completely for his time that, beyond participating in the administrative work of the scientific societies with which he was connected, he took but little part in extraneous affairs. He was not particularly of a business turn of mind in the commercial sense, and during his industrial career his brother Thomas was the chief man of business connected with the factory. One line of work distinct from his purely scientific occupations is, however, worthy of special record, because it enabled him to exert some influence in the cause of technical and scientific education. His family had for a long period been connected with the Leathersellers' Company, and through this connection he was enabled to promote the cause of chemical research and also to become, as the representative of his Company, a member of the governing body of the City and Guilds of London Institute, whose meetings he attended with considerable regularity, although, unless specially appealed to, he seldom took part in the discussions at the Council table. But his influence in the City of London, although unobtrusive, was of a most beneficial character, and every movement for the promotion of science and of scientific education was certain to receive his support. His special knowledge of the requirements of the chemical technologist and his sympathy with the teaching staffs have contributed in no small degree to promote the cause of sound chemical education in London through the City and Guilds Institute. As an illustration of the modesty of his character, it may be of interest to relate that many of his

colleagues in the City were unaware, until the Jubilee of 1906, that the William Perkin who sat at their meetings was the same man who, half a century before, had laid the foundations of a great industry. The following details concerning his connection with the Leathersellers have been supplied by the late Mr. W. Arnold Hepburn, the Clerk to the Company :—

- “ William Henry Perkin, son of George Fowler Perkin, was made free by patrimony, November 13, 1861.
- “ George Fowler Perkin, son of Thomas Perkin, was made free by patrimony, February 4, 1829.
- “ Thomas Perkin, apprenticed to Isaac Roberts, March 16, 1772, was made free by servitude, July 7, 1790.
- “ William Henry Perkin served the office of Steward, 1881–2; 4th Warden, 1885–6; 2nd Warden, 1895–6; Master, 1896–7.
- “ During the Mastership of Dr. Perkin in 1896 the Company, at his instance, resolved to found a Research Fellowship in Chemistry as applied to Manufactures, tenable at the Central Technical College of the City and Guilds Institute, and to grant £150 a year in support thereof.”

A portrait of Perkin in his robe as LL.D. of the University of St. Andrews, painted by Henry Grant in 1898, is on the wall at the Leathersellers' Hall in St. Helen's Place.

Although his single-minded devotion to his researches and his retiring nature caused Perkin to remain in comparative obscurity from the point of view of the general public, his real worth was well known to, and received frequent recognition from, his scientific colleagues. In this respect his history is that of the majority of active workers in the field of science in this country who do not wield the pen as *littérateurs*, or whose achievements are not of a sufficiently startling kind to create public notoriety. With the passing of the generation which witnessed the interest aroused by the discovery of mauve, and which was fanned into temporary excitement by the sensational accounts circulated by the newspapers of the period, the memory of Perkin faded from the public mind. To most of his fellow countrymen the memorable international gathering in London in 1906 came as a revelation that they could claim as their compatriot the man whom all the nations had sent their representatives to honour as an individual, and in celebration of the fiftieth anniversary of the discovery of the first of the synthetic dye-stuffs.

Perkin was elected into the Royal Society in 1866; he served on the Council in 1879–81, and again in 1892–94. In 1893–94 he was made one of the Vice-Presidents. He joined the Chemical Society in 1856, served on the Council in 1861–62, and in 1868–69; was Secretary, from 1869 to 1883, and President from 1883 to 1885. By way of Academic distinctions he received the degree of Ph.D. from the University of Würzburg in 1882; the degree of LL.D. from the University of St. Andrews in 1891; and was made

a D.Sc. of Victoria University in 1904. In connection with the Jubilee of 1906, the University of Heidelberg conferred upon him the degree of Ph.D., the Munich Technical High School awarded him the diploma of Dr. Ing., and the same year the Universities of Oxford and Leeds gave him the degree of D.Sc. During his subsequent visit to America in the autumn of 1906, in connection with the celebrations organised in that country, he received the degree of D.Sc. from Columbia University, and LL.D from the Johns Hopkins University, of Baltimore, the latter degree having been most appropriately conferred by his chemical colleague, President Ira Remsen.

He was President of the Society of Chemical Industry in 1884-85, at the time of his death was President of the Society of Dyers and Colourists,* and had recently accepted office as President of the Faraday Society. In 1884 he was made an Honorary Foreign Member of the German Chemical Society. Following the early recognition of his technological work by the "Société Industrielle de Mulhouse," already referred to, he received from the Royal Society a Royal Medal in 1879, and the Davy Medal in 1889; from the Chemical Society the Longstaff Medal in 1888; from the Society of Arts the Albert Medal in 1890; from the Institution of Gas Engineers the Birmingham Medal in 1892, and the Gold Medal of the Society of Chemical Industry in 1898. At the Jubilee Celebration in 1906, Professor Emil Fischer, on behalf of the German Chemical Society, presented him with the Hofmann Medal, and Professor Haller, on behalf of the Chemical Society of Paris, with the Lavoisier Medal.

The influence which Perkin has exerted upon this generation is not to be measured solely by his achievements in pure and applied chemistry. His life was noble in its simplicity and his single-minded devotion to his work, combined with a character known to be religious in the highest and best sense of the term, will bequeath to posterity an enduring example of humility in the face of success which would have marred many men of smaller moral calibre. The financial success of his early manufacturing experience was turned to account simply as a means of advancing science, and no distinction which he ever gained throughout a career which culminated in 1906, when the King conferred upon him the honour of Knighthood, and when the nations of the world assembled to render him homage, had the slightest influence upon the modesty and gentleness of his disposition. It was his personality that caused him to be revered in his domestic circle, and to be beloved by all who enjoyed the privilege of his friendship. Two of the addresses presented at the jubilee meeting in

* In honour of the founder of the industry this Society has established a Perkin Medal "for inventions of striking scientific or industrial merit, applicable to, or connected with, the tinctorial industries." Perkin's last official act in connection with this Society was to accompany a deputation to the Dyers' Company asking the latter to contribute towards the foundation of a prize for the encouragement of research in tinctorial chemistry. The American Memorial Committee also founded a Perkin medal for American chemists in 1906 in connection with their Jubilee Celebration in New York.

1906 give striking expression to the universal esteem in which he was held as a man :—

“But however highly your technical achievements be rated, those who have been intimately associated with you must feel that the example which you have set by your rectitude, as well as by your modesty and sincerity of purpose, is of chiefest value.” (From the address presented by the Chemical Society.)

“You have given to science the allegiance of a noble life, and you have not allowed the seductions of wealth to abate the loyalty of your devotion to truth and knowledge. This is an example for which the age owes you unstinted thanks. . . . Amid these varied activities it is pleasant to know that you have cultivated the full humanity of life. Music and art have found in you a devoted disciple, and in the family and social relationship of life you have shown that science gives a truer interpretation of, and a deeper meaning to, all that is sacred and good in the heart of man.” (From the address presented by the Society of Dyers and Colourists.)

Perkin was twice married, his first wife being a daughter of the late Mr. John Lisset; some years after her death he married the daughter of Mr. Herman Mollwo. Lady Perkin, three sons, all of whom have made their mark as chemists, and four daughters survive. Two of his sons, William Henry and Arthur George, were elected into the Royal Society in 1890 and 1906 respectively, and it was always a source of great satisfaction to him to know that all his sons were following in his footsteps. In his general mode of life Perkin was a man of extreme frugality, robust and active to the last. To one of his retiring habits the strain accompanying the jubilee celebrations in 1906 and the subsequent ordeal of his American tour must have been considerable, but he bore all the excitement and fatigue without the least indication of discomfort. Literally he died in harness; a few months previously he had read his last paper before the Chemical Society, and he was looking forward to being able to resume his research work quietly and uninterruptedly after the distractions of 1906. The illness which brought his noble and useful life to an end, which, in view of his activity, cannot but be regarded as premature, did not at first reveal any serious symptoms. The writer of this notice was with him a few hours before his death, and although he complained of suffering pain he spoke hopefully of his condition and anticipated being soon able to leave his room. The illness proved, however, to be more serious than he or his family were aware of; a sudden change for the worse occurred, and on July 14, 1907, he passed away in perfect peace and in the full tide of well-won honour.

R. M.

H. C. RUSSELL, 1836—1907.

HENRY CHAMBERLAINE RUSSELL, a son of the Honourable Bourne Russell, was born in 1836 at West Maitland, New South Wales. He was educated at the West Maitland Grammar School, and graduated at the Sydney University in 1858, obtaining the Deas-Thomson scholarship for physics and chemistry. On leaving the university he became assistant at the Sydney Observatory, and in 1870 was appointed Government Astronomer, a post he occupied till his retirement in 1905.

Astronomy in Australia began with the foundation of the Paramatta Observatory by Sir Thomas Brisbane in 1822. Valuable work was carried out by Dunlop and Rumker, but the observatory only continued in operation for a short time, and was dismantled in 1847. For ten years Australia had no observatory, but shortly after the arrival of Sir W. T. Dennison as Governor-General of New South Wales, £7000 was set apart for the building of an astronomical observatory in the colony. On the advice of Sir George Airy, Mr. W. Scott, Fellow and Mathematical Lecturer of Sidney Sussex College, Cambridge, was appointed Government Astronomer. After spending a few months at Greenwich, Mr. Scott arrived at Sydney on November 1, 1856. He chose the best site available for the observatory, on one of the many headlands projecting into Sydney Harbour, and erected a good stone building containing a transit room, an 18-foot dome, and a tower high enough for the time-ball to be visible from the greater part of the harbour and the city. The transit instrument was an old one which had been in use at Paramatta, but a good equatorial, with a $7\frac{1}{4}$ -inch object-glass by Merz, was obtained in 1860. Mr. Scott resigned in 1862, and, after a few months, during which Mr. Russell was Acting Director of the observatory, was succeeded by Mr. Smalley, who was Government Astronomer till his death in 1870.

Immediately on his appointment, in 1870, Mr. Russell commenced to reorganise the instrumental equipment of the observatory. He was well fitted for this task by his mechanical skill and inventiveness, qualities of special value in a country where the fine mechanical work required in the manufacture of scientific instruments was then practically unknown. The observatory buildings were enlarged, a new reversible transit circle, with an object-glass of $6\frac{1}{2}$ inches, was obtained, and, in 1874, a large equatorial, with an object-glass of $11\frac{1}{2}$ inches. The mounting of this instrument, the driving clock, and the dome containing it were made from Mr. Russell's designs. With this instrument a large number of valuable observations of double stars, clusters, and nebulae have been continuously made by Mr. Russell and his assistants.

Preparations for observation of the transit of Venus in 1874 were begun by Mr. Russell in 1870, as the favourable position of the eastern coast of Australia for observation of egress made it desirable that as extensive a

programme as practicable should be carried out. In 1872 the Government of New South Wales voted £1000 for the purpose, and with this sum Mr. Russell proceeded to equip four observing stations. Owing to the short time available, many of the instruments were made in the colony, the more delicate parts under the direct supervision of Mr. Russell. The observations were, generally speaking, very successful, and an interesting account of them was published by Mr. Russell in 1892.

The application of photography to astronomy attracted Mr. Russell; in 1887 he attended the Astrographic Congress at Paris, and promised the co-operation of the Sydney Observatory. In the same year the purchase of a photographic objective of 13 inches aperture was sanctioned; but as the mounting could be made in Sydney with needful accuracy, it was arranged that this should be made in the colony. The equatorial mounting, the driving clock, and various accessories of the instrument were accordingly made from Mr. Russell's designs. The mounting was finished in 1890, before the object-glass arrived from Europe, and the interval was employed in taking photographs of nebulae and other interesting objects of the southern skies with a Dallmeyer portrait lens of 6 inches aperture and 32 inches focus. It was found that in the neighbourhood of the city there was sufficient diffused light to produce fogging when long exposures were given. Accordingly, at Mr. Russell's instance, seven acres of land near the Pennant Hills were obtained from the Government, and the instrument and necessary buildings were erected there.

The portion of the Astrographic Catalogue undertaken by the Sydney Observatory extends from 54° to 62° of S. declination. This work, involving the taking and measurement of 1400 photographic plates and the observation of the reference stars at the meridian instrument, was actively carried on under Mr. Russell's direction till the time of his retirement. In connection with this work, he devised an electric control for the driving clock of the equatorial and designed a machine for the measurement of the photographic plates.

Mr. Russell was interested in meteorology no less than in astronomy. At the time of his appointment, in 1870, there were in New South Wales less than a dozen stations where meteorological observations were made. At the time of his retirement he had increased the number to 1800. The returns from these stations were compiled and analysed at the observatory, and published annually under the title, "Results of Rain, River, and Evaporation Observations made in New South Wales." In conjunction with his colleagues at Melbourne and Adelaide, telegraphic exchanges of weather reports were organised, and these were utilised by him for the issue of daily weather forecasts. These predictions, which have been issued since 1887, are stated to be correct in from 80 to 84 per cent. of times, and are of special value in the wheat-producing districts and other country centres.

In 1877 Mr. Russell published an exhaustive treatise on the climate of New South Wales. The historical part of this work presented great

difficulties, "the facts being buried under a thousand times their bulk of other matter." From all sources available, including authorities living at the time, he endeavoured to ascertain meteorological data in any particular year or period in the history of the colony. In this way he produced a work of reference on the droughts, floods, and climatic conditions of New South Wales from the times of the first settlers.

In these researches Mr. Russell was animated by the desire to discover in meteorological data some period which would connect them with cosmical phenomena. He wrote several papers on Weather Periodicity and considered he had found evidence for a cycle of 19 years. Whatever views be taken of this, it cannot be denied that his papers contain much valuable systematised meteorological information.

In 1879 Mr. Russell communicated to the Royal Society of New South Wales a short paper entitled "The River Darling: the water which should pass through it." He predicted the occurrence of an unlimited supply of good water in the Darling district, to be derived from the vast supplies of rain water which must sink into the ground to flow at some lower level. This prediction of Mr. Russell's, made at a time when nothing was known of the existence of artesian water in the western plains of New South Wales, was made in reliance on his carefully compiled meteorological data. His colleague in the University of Sydney, Professor David, cites this as an example of the scientific imagination with which Mr. Russell was gifted, leading him to picture results which followed from the phenomena he was considering.

Mr. Russell found in meteorology, no less than in astronomy, scope for his inventiveness. The electric barograph, the recording anemometer and pluviometer of the observatory were designed and largely made by him. They are still in work after 30 years of use.

In 1888 Mr. Russell printed and distributed papers to captains of vessels, with instructions that after the date, latitude, and longitude had been inserted, they should be sealed in bottles and allowed to drift. A number were sooner or later picked up and forwarded to Mr. Russell. From the data thus secured he deduced results as to the velocity and direction of the currents in the Southern Ocean and particularly round the Australian coast. These he communicated to the Royal Society of New South Wales in a series of short "Current Papers." To the same Society he contributed two important papers on Icebergs in the Southern Ocean. The measurement of tides was also taken up by Mr. Russell, and the self-recording tide gauge of Sydney Harbour was made from his design in 1873.

Although Mr. Russell's scientific interests ranged over the wide fields of astronomy, meteorology, and physical geography, he, nevertheless, took an active part in educational questions, particularly in the organisation of technical education in New South Wales. At the time of his death he was the oldest Fellow of the Senate of the University of Sydney and had been Vice-Chancellor in the year 1891. He was four times President of the Royal

Society of New South Wales and was the first President of the Australasian Association for the Advancement of Science. He was elected a Fellow of the Royal Society in 1886. In 1890 he was created Companion of the Order of St. Michael and St. George.

Mr. Russell had a severe illness in 1903, from the effects of which he never entirely recovered. He died on February 22, 1907, and leaves a widow, four daughters and one son.

F. W. D.



MINUTES OF MEETINGS.—SESSION 1907-8.

November 7, 1907.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following papers were read :—

- I. "The Effect of Pressure upon the Arc Spectra of Metals." By W. GEOFFREY DUFFIELD. Communicated by Professor SCHUSTER, F.R.S.
- II. "The Electric Discharge in Monatomic Gases." By F. SODDY and T. D. MACKENZIE. Communicated by Professor LARMOR, Sec. R.S.
- III. "The Diurnal Variation of Terrestrial Magnetism." By Professor A. SCHUSTER, F.R.S.
- IV. "On the Measurement of Temperatures in the Cylinder of a Gas Engine." By Professor H. L. CALLENDAR, F.R.S., and Professor W. E. DALBY.
- V. "Note on the Association of Helium and Thorium in Minerals." By the Hon. R. J. STRUTT, F.R.S.
- VI. "Further Results of the Experimental Treatment of Trypanosomiasis in Rats." (Progress Report of Sleeping Sickness Committee of the Royal Society.) By H. G. PLIMMER and J. D. THOMSON.

November 14, 1907.

Professor DAVID FERRIER, Vice-President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

Mr. S. H. Burbury, Dr. A. E. H. Tutton, and Mr. H. B. Woodward were elected Auditors of the Treasurer's accounts on the part of the Society.

In pursuance of the Statutes, notice of the ensuing Anniversary Meeting was given from the Chair.

The following papers were read :—

- I. "On the Cranial and Facial Characters of the Neandertal Race." By Professor W. J. SOLLAS, F.R.S.

- II. "Some Features in the Hereditary Transmission of the Self-black and the 'Irish' Coat Characters in Rats." By G. P. MUDGE. Communicated by Dr. A. D. WALLER, F.R.S.
- III. "On the Inheritance of Eye-colour in Man." By C. C. HURST. Communicated by W. BATESON, F.R.S.
- IV. "On the Result of Crossing Round with Wrinkled Peas, with especial reference to their Starch Grains." By A. D. DAREISHIRE. Communicated by Professor J. B. FARMER, F.R.S.
- V. "On the Rate of Elimination of Chloroform from the Blood after Anaesthesia." By G. A. BUCKMASTER and J. A. GARDNER. Communicated by Dr. A. D. WALLER, F.R.S.
- VI. "Implantation of Actively Proliferating Epithelium." By Dr. J. O. WAKELIN BARRATT. Communicated by Professor C. S. SHERRINGTON, F.R.S.

November 21, 1907.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

In pursuance of the Statutes, notice of the ensuing Anniversary Meeting was given from the Chair, and the list of the Officers and Council for the ensuing year proposed by the Council for election was read as follows :—

President.—The Right Hon. the Lord Rayleigh, O.M., M.A., D.C.L.

Treasurer.—Alfred Bray Kempe, M.A.

Secretaries.— { Professor Joseph Larmor, D.Sc., D.C.L., LL.D.
 { Sir Archibald Geikie, K.C.B., D.C.L., Sc.D., LL.D.

Foreign Secretary.—Professor John Rose Bradford, M.D., D.Sc.

Other Members of the Council.—Henry Frederick Baker, Sc.D. ; the Right Hon. Arthur James Balfour, D.C.L. ; Sir William Crookes, D.Sc. ; Francis Darwin, M.B. ; Sir George Howard Darwin, K.C.B. ; Professor James Cossar Ewart, M.D. ; Professor David Ferrier, M.D. ; Charles Thomas Heycock, M.A. ; Professor Sydney J. Hickson, D.Sc. ; Professor John Joly, D.Sc. ; the Hon. Charles Algernon Parsons, C.B. ; Alexander Scott, D.Sc. ; Albert Charles Seward, M.A. ; Professor Frederick Thomas Trouton, Sc.D. ; Augustus Désiré Waller, M.D. ; William Whitaker, B.A.

The following papers were read :—

- I. "Results of the Interaction of Mercury with Alloys of other Metals." By Dr. J. W. MALLET, F.R.S.
 - II. "Note on the Sensibility of the Ear to the Direction of Explosive Sounds." By A. MALLOCK, F.R.S.
 - III. "On the Silver Voltameter." By F. E. SMITH, T. MATHER, F.R.S., and Dr. T. M. LOWRY. Part I.—A Comparison of various Forms of Silver Voltameters, by F. E. Smith ; and a Determination of the Electro-chemical Equivalent of Silver, by F. E. Smith and T. Mather, F.R.S. Part II.—The Chemistry of the Silver Voltameter, by F. E. Smith and T. M. Lowry. Communicated by Dr. GLAZEBROOK, F.R.S.
 - IV. "On the Normal Weston Cadmium Cell." By F. E. SMITH. Communicated by Dr. GLAZEBROOK, F.R.S.
 - V. "On a Method of Depositing Copper upon Glass from Aqueous Solutions in a Thin Brilliantly Reflecting Film, and thus producing a Copper Mirror." By Dr. F. D. CHATTAWAY, F.R.S.
 - VI. "On Luminous Efficiency and the Mechanical Equivalent of Light." By Dr. C. V. DRYSDALE. Communicated by Professor S. P. THOMPSON, F.R.S.
 - VII. "The Dispersion of Double Refraction in Relation to Crystal Structure." By Dr. T. H. HAVELOCK. Communicated by Professor LARMOR, Sec. R.S.
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November 30, 1907.

ANNIVERSARY MEETING.

Lord RAYLEIGH, O.M., D.C.L., President, in the Chair.

The Report of the Auditors of the Treasurer's accounts was read, and the thanks of the Society were given to the Treasurer and to the Auditors.

The List of Fellows deceased and the List of Fellows elected into the Society since the last Anniversary were read.

The Report to the Society from the Council, upon the work during the past year, was, upon the motion of the President, received.

The President delivered his Anniversary Address.

On the motion of Sir William Macewen, seconded by Sir W. T. Thiselton-Dyer, the thanks of the Society were voted to the President for his address.

The Awards of the Medals for the year were announced as follows, and the Medals were presented from the Chair :—

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| The Copley Medal | To Professor A. A. Michelson. |
| A Royal Medal | „ Dr. Ramsay H. Traquair. |
| A Royal Medal | „ Dr. E. W. Hobson. |
| The Davy Medal..... | „ Professor E. W. Morley. |
| The Buchanan Medal... | „ Mr. W. H. Power. |
| The Sylvester Medal... | „ Professor W. Wirtinger. |
| The Hughes Medal..... | „ Professor E. H. Griffiths. |

The President having, with the consent of the Society, nominated Admiral A. M. Field and Professor A. M. Worthington as Scrutators, to assist the Secretaries in examining the balloting lists for the election of Council and Officers, the votes of the Fellows present were taken. The Scrutators reported that the Council and Officers nominated at the preceding meeting had been duly elected, and their names were accordingly announced from the Chair.

The thanks of the Society were given to the Scrutators.

The following Fellows were present and voted :—

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| A. W. Alcock. | F. S. Kipping. |
| C. W. Andrews. | G. W. Lamplugh. |
| H. E. Armstrong. | E. R. Lankester. |
| W. E. Ayrton. | J. Larmor. |
| H. F. Baker. | A. E. H. Love. |
| A. B. Basset. | W. Macewen. |
| H. T. Brown. | H. McLeod. |
| D. Bruce. | R. Meldola. |
| C. Chree. | A. Pedler. |
| S. Copeman. | W. J. Pope. |
| P. H. Cowell. | E. B. Poulton. |
| E. W. Creak. | Rayleigh. |
| F. Darwin. | A. W. Rücker. |
| G. H. Darwin. | E. Rutherford. |
| W. Duddell. | A. Scott. |
| W. R. Dunstan. | D. H. Scott. |
| F. W. Dyson. | W. N. Shaw. |
| J. Evans. | T. R. R. Stebbing. |
| D. Ferrier. | S. P. Thompson. |
| A. M. Field. | J. I. Thornycroft. |
| A. Gamgee. | W. A. Tilden. |
| A. Geikie. | R. H. Traquair. |
| D. Gill. | A. E. H. Tutton. |
| R. T. Glazebrook. | V. H. Veley. |
| F. Gotch. | W. H. White. |
| C. E. Groves. | A. N. Whitehead. |
| W. Heape. | H. A. Wilson. |
| G. J. Hinde. | W. E. Wilson. |
| H. H. Howorth. | H. B. Woodward. |
| J. H. Jackson. | A. M. Worthington. |
| A. B. Kempe. | W. H. Young. |

December 5, 1907.

Lord RAYLEIGH, O.M., D.C.L., President, followed by Dr. Ferrier, Vice-President, in the Chair.

A List of the Presents received was laid on the Table, and thanks ordered for them.

The President announced that he had appointed as Vice-Presidents—

The Treasurer.
Sir William Crookes.
Mr. Francis Darwin.
Dr. Ferrier.

Professor Michelson (Copley Medallist) gave a demonstration of some optical experiments.

The following Papers were read :—

- I. "Reciprocal Innervation of Antagonistic Muscles. 11th Note.—Further Observations on 'Successive Induction.'" By Professor C. S. SHERRINGTON, F.R.S.
- II. "On the Distribution of the Different Arteries Supplying the Human Brain." By Dr. C. E. BEEVOR. Communicated by Professor D. FERRIER, F.R.S.
- III. "Localisation of Function in the Lemur's Brain." By Dr. F. W. MOTT, F.R.S., and Professor W. D. HALLIBURTON, F.R.S.
- IV. "On the Supposed Extracellular Photosynthesis of Carbon Dioxide by Chlorophyll." By Professor A. J. EWART. Communicated by Professor J. B. FARMER, F.R.S.
- V. "The Influence of Increased Barometric Pressure on Man. No. 4.—The Relation of Age and Body Weight to Decompression Effects." By L. HILL, F.R.S., and M. GREENWOOD, Junr.
- VI. "On the Present Distribution and Origin of the Calcareous Concretions in Coal Seams known as 'Coal Balls.'" By Miss STOPES and D. M. S. WATSON. Communicated by J. J. H. TEALL, F.R.S.
- VII. "On the Structure of *Sigillaria Scutellata*, Brongn., and other Eusigillarian Stems, in Comparison with those of other Palæozoic Lycopods." By E. A. NEWELL ARBER and H. H. THOMAS. Communicated by Dr. D. H. SCOTT, F.R.S.

December 12, 1907.

Lord RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the Table, and thanks ordered for them.

The following Papers were read :—

- I. "Further Consideration of the Stability of the Pear-shaped Figure of a Rotating Liquid." By Sir G. H. DARWIN, K.C.B., F.R.S.
- II. "Preliminary Note on the Operational Invariants of a Binary Quantic." By Major P. MACMAHON, F.R.S.

- III. "The Action of Ozone on Water-colour Pigments." By Sir W. ABNEY, K.C.B., F.R.S.
- IV. "On Kinetic Stability." By Professor H. LAMB, F.R.S.
- V. "The Absorption Spectra of the Vapour of Benzene, and its Homologues, at different Temperatures and Pressures, and likewise of Solutions of Benzene." By Professor W. N. HARTLEY, F.R.S.
- VI. "The Spectrum of Magnesium and of the So-called Magnesium Hydride as obtained by Spark Discharges under Reduced Pressure." By E. E. BROOKS. Communicated by Sir W. CROOKES, F.R.S.
- VII. "Magnetic Declination at Kew Observatory, 1890 to 1900." By Dr. C. CHREE, F.R.S.
- VIII. "The Effects of Temperature and Pressure on the Thermal Conductivities of Solids. Part II.—The Effect of Low Temperatures on the Thermal Conductivities of Pure Metals and Alloys." By Professor C. H. LEES, F.R.S.
- IX. "On Exterior Ballistics (No. 2)." By Professor G. FORBES, F.R.S.
- X. "On the Scattering of the β -Rays from Uranium by Matter." By J. A. CROWTHER. Communicated by Professor J. J. THOMSON, F.R.S.

The Society adjourned over the Christmas Vacation to Thursday, January 16, 1908.

January 16, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

In pursuance of the Statutes, the names of the Candidates for election into the Society were read as follows :—

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| Adeney, Walter Ernest. | Grace, John Hilton. |
| Anderson, Tempest. | Gray, Thomas. |
| Arnold, John Oliver. | Green, Arthur George. |
| Baly, Edward Charles Cyril. | Hadfield, Robert Abbott. |
| Barlow, Sir Thomas. | Hall, Alfred Daniel. |
| Barlow, William. | Hamilton, David James. |
| Barnes, Rev. Ernest William. | Harden, Arthur. |
| Barnes, Howard Turner. | Hardy, Godfrey Harold. |
| Bather, Francis Arthur. | Harker, John Allan. |
| Beare, T. Hudson. | Harmer, Frederic William. |
| Berkeley, Earl of. | Haycraft, John Berry. |
| Blakesley, Thomas Holmes. | Hewitt, John Theodore. |
| Bolton, Charles. | Hoyle, William Evans. |
| Braithwaite, Robert. | Innes, Robert Thorburn Ayton. |
| Bruce, John Mitchell. | Jones, Humphrey Owen. |
| Bulloch, William. | Jukes-Browne, Alfred John. |
| Chattock, Arthur Prince. | Kerr, John Graham. |
| Clerk, Dugald. | Knott, Cargill Gilston. |
| Cohen, Julius Berend. | Lapworth, Arthur. |
| Cole, Grenville Arthur James. | Leathes, John Beresford. |
| Crompton, Rookes Evelyn B. | Leishman, William Boog. |
| Cunningham, Joseph T. | Lewis, William James. |
| Dalby, William Ernest. | Lockyer, William James Stewart. |
| Dean, George. | Macdonald, John Smythe. |
| Dendy, Arthur. | McFadyean, Sir John. |
| Dixey, Frederick Augustus. | Maclaurin, Richard Cockburn. |
| Dixon, Henry H. | Major, Charles Immanuel Forsyth. |
| Dixon, Walter Ernest. | Marsh, Howard. |
| Donnan, Frederick George. | Masterman, Arthur Thomas. |
| Filon, Louis Napoleon George. | Matthey, Edward. |
| Forbes, Henry Ogg. | Maunder, Edward Walter. |
| Fox, Francis. | Morgan, Gilbert Thomas. |
| Gardiner, John Stanley. | Morley, Frank. |
| Garrod, Archibald Edward. | Morris, Henry. |
| Garwood, Edmund Johnston. | Nevill, Edmund Neville. |
| Gowland, William. | Oliver, George. |

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| Paton, Diarmid Noël. | Smith, James Lorrain. |
| Pembrey, Marcus Seymour. | Stapf, Otto. |
| Plimmer, Henry G. | Stoney, George Gerald. |
| Pocock, Reginald Innes. | Stromeyer, Johann Phillip E. C. |
| Porter, Alfred William. | Swinton, Alan Archibald Campbell. |
| Prior, George Thurland. | Thorpe, Jocelyn Field. |
| Rendle, Alfred Barton. | Treves, Sir Frederick. |
| Rivers, William Halse Rivers. | Vernon, Horace Middleton. |
| Rogers, Leonard. | Walker, James. |
| Russell, Hon. Bertrand A. W. | Willis, John Christopher. |
| Scharff, Robert Francis. | Wilson, Ernest. |
| Sclater, William Lutley. | Wilson, James Thomas. |
| Shattock, Samuel George. | Young, Alfred H. |

The following Papers were read :—

- I. "Alternate Current Measurement." By Dr. W. E. SUMPNER.
Communicated by Professor J. PERRY, F.R.S.
- II. "Prominence and Coronal Structure." By Dr. W. J. S. LOCKYER. Communicated by Sir NORMAN LOCKYER, K.C.B., F.R.S.
- III. "The Conversion of Diamond into Coke in High Vacuum by Cathode Rays." By Hon. C. A. PARSONS, C.B., F.R.S., and A. A. CAMPBELL SWINTON.
- IV. "On the Perception of the Direction of Sound." By Professor C. S. MYERS and Professor H. A. WILSON, F.R.S.
- V. "Preliminary Note on Certain Phenomena of the Electric Discharge through Rarefied Nitrogen." By Dr. G. J. BURCH, F.R.S., J. E. MARSH, F.R.S., and R. DE J. F. STRUTHERS.

January 23, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, followed by
Sir WILLIAM CROOKES, Vice-President, in the Chair.

A List of the Presents received was laid on the table, and thanks
ordered for them.

The following Papers were read :—

- I. "The Charges on Positive and Negative Ions in Gases." By
Professor J. S. TOWNSEND, F.R.S.
- II. "Report on the Eruptions of the Soufrière in St. Vincent in
1902 and on a Visit to Montagne Pelée in Martinique.
Part II.—The Changes in the Districts and the Subsequent
History of the Volcanoes." By Dr. TEMPEST ANDERSON.
Communicated by Professor T. G. BONNEY, F.R.S.

- III. "Petrographical Notes on the Products of the Eruptions of May, 1902, at the Soufrière in St. Vincent." By Dr. J. S. FLETT. Communicated by H. B. WOODWARD, F.R.S.
- IV. "On the Intimate Structure of Crystals. Part VI.—Titanic Oxide, its Polymorphs and Isomorphs." By Professor W. J. SOLLAS, F.R.S.
- V. "Dietetics in Tuberculosis; Principles and Economics." By Dr. N. D. BARDSWELL and J. E. CHAPMAN. Communicated by Sir T. CLIFFORD ALLBUTT, K.C.B., F.R.S.
- VI. "The Origin and Destiny of Cholesterol in the Animal Organism. Part I.—On the So-called Hippocoprosterol." By C. DORÉE and J. A. GARDNER. Communicated by Dr. A. D. WALLER, F.R.S.

January 30, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "On the Observation of Sun and Stars made in some British Stone Circles. Third Note.—The Aberdeenshire Circles." By Sir NORMAN LOCKYER, K.C.B., F.R.S.
 - II. "On the Non-periodic or Residual Motion of Water moving in Stationary Waves." By Mrs. AYRTON. Communicated by Professor J. H. POYNTING, F.R.S.
 - III. "The Refractive Index and Dispersion of Light in Argon and Helium." By W. BURTON. Communicated by Professor J. J. THOMSON, F.R.S.
 - IV. "On the Generation of a Luminous Glow in an Exhausted Receiver moving near an Electrostatic Field, and the Action of a Magnetic Field on the Glow so produced." By the Rev. F. J. JERVIS-SMITH, F.R.S.
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February 6, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "On the Weight of Precipitum obtainable in Precipitin Interactions with Small Weights of Homologous Protein." By Professor D. A. WELSH and H. G. CHAPMAN. Communicated by Dr. C. J. MARTIN, F.R.S.
- II. "Nitrification in Acid Soils." By A. D. HALL, N. H. J. MILLER, and C. T. GIMINGHAM. Communicated by Professor H. E. ARMSTRONG, F.R.S.
- III. "A Criticism of the Opsonic Theory, based upon Studies carried out by means of Melanin." By S. G. SHATTOCK and L. S. DUDGEON. Communicated by Professor J. ROSE BRADFORD, For. Sec., R.S.
- IV. "A Contribution to the Study of the Mechanism of Respiration, with especial reference to the Action of the Vertebral Column and Diaphragm." By J. F. HALLS DALLY. Communicated by Sir T. CLIFFORD ALLBUTT, K.C.B., F.R.S.

February 13, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "The Constitution of the Electric Spark." By T. ROYDS. Communicated by Professor A. SCHUSTER, F.R.S.
- II. "On the Determination of Viscosity at High Temperatures." By Dr. C. E. FAWSITT. Communicated by Professor A. GRAY, F.R.S.
- III. "The Effect of Hydrogen on the Discharge of Negative Electricity from Hot Platinum." By Professor H. A. WILSON, F.R.S.
- IV. "The Decomposition of Ozone by Heat." By Dr. E. P. PERMAN and R. H. GREAVES. Communicated by Professor E. H. GRIFFITHS, F.R.S.

February 20, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "Notes on the Application of Low Temperatures to some Chemical Problems. I.—Use of Charcoal in Vapour Density Determinations. II.—Rotatory Power of Organic Substances." By Sir JAMES DEWAR, F.R.S., and Dr. H. O. JONES.
- II. "On the Osmotic Pressure of Compressible Solutions of any Degree of Concentration. Part II.—Cases in which both Solvent and Solute are Volatile." By A. W. PORTER. Communicated by Professor F. T. TROUTON, F.R.S.
- III. "Effects of Self-induction in an Iron Cylinder when Traversed by Alternating Currents." By Professor ERNEST WILSON, Communicated by Sir W. H. PREECE, K.C.B., F.R.S.
- IV. "On the Refractive Indices of Gaseous Nitric Oxide, Sulphur Dioxide, and Sulphur Trioxide." By C. CUTHBERTSON and E. P. METCALFE. Communicated by Professor F. T. TROUTON, F.R.S.
- V. "On the Dispersion of Gaseous Mercury, Sulphur, Phosphorus, and Helium." By C. CUTHBERTSON and E. P. METCALFE. Communicated by Professor F. T. TROUTON, F.R.S.

February 27, 1908.

Mr. FRANCIS DARWIN, Vice-President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "The Influence of Temperature on Phagocytosis." By J. C. G. LEDINGHAM. Communicated by C. J. MARTIN, F.R.S.
- II. "The Glycogenic Changes in the Placenta and the Fetus of the Pregnant Rabbit.—A Contribution to the Chemistry of Growth." By J. LOCHHEAD and W. CRAMER. Communicated by Professor E. A. SCHÄFER, F.R.S.
- III. "On the Maturation of the Ovum in the Guinea-pig." By Professor J. E. S. MOORE and Miss F. TOZER. Communicated by Professor J. B. FARMER, F.R.S.

March 5, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

In pursuance of the Statutes, the names of the Candidates recommended by the Council for election into the Society were read from the Chair as follows :—

| | |
|-------------------------|-------------------------------|
| Barlow, William. | Grace, John Hilton. |
| Berkeley, Earl of. | Hamilton, David James. |
| Clerk, Dugald. | Major, C. Immanuel Forsyth. |
| Dendy, Arthur. | Nevill, Edmund Neville. |
| Dixon, Henry H. | Rivers, William Halse Rivers. |
| Gardiner, John Stanley. | Russell, Hon. Bertrand A. W. |
| Gowland, William. | Stapf, Otto. |

Thorpe, Jocelyn Field.

Dr. T. E. Thorpe described to the Society the results of his further observations on the Atomic Weight of Radium in continuation of the account presented to the Society in the Bakerian Lecture delivered June 20, 1907.

The following Papers were read :—

- I. "On the Electrical Resistance of Moving Matter." By Professor F. T. TROUTON, F.R.S., and A. O. RANKINE.
- II. "On the Nature of the Streamers in the Electric Spark." By Dr. S. R. MILNER. Communicated by Professor W. M. HICKS, F.R.S.
- III. "The Relation between Wind Velocity at 1000 Metres Altitude and the Surface Pressure Distribution." By E. GOLD. Communicated by Dr. W. N. SHAW, F.R.S.

March 12, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "Description of the Brain of Mr. Charles Babbage, F.R.S." By Sir VICTOR HORSLEY, F.R.S.

- II. "The Origin and Destiny of Cholesterol in the Animal Organism. Part II.—The Excretion of Cholesterol by the Dog." By C. DORÉE and J. A. GARDNER. Communicated by Dr. A. D. WALLER, F.R.S.
- III. "On Reciprocal Innervation in Vaso-motor Reflexes and the Action of Strychnine and of Chloroform thereon." By Dr. W. M. BAYLISS, F.R.S.
- IV. "Bacteria as Agents in the Oxidation of Amorphous Carbon." By Professor M. C. POTTER. Communicated by Professor J. B. FARMER, F.R.S.
- V. "The Life-history of *Trypanosoma equiperdum*." By Professor J. E. SALVIN-MOORE and ANTON BREINL. Communicated by Sir RUBERT BOYCE, F.R.S.

March 19, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "On Vapour-Pressure and Osmotic Pressure of Strong Solutions." By Professor H. L. CALLENDAR, F.R.S.
- II. "On Secondary β -Rays." By Professor J. A. MCCLELLAND. Communicated by Professor J. JOLY, F.R.S.
- III. "On the Measurement of the Atmospheric Electric Potential Gradient and the Earth-Air Current." By C. T. R. WILSON, F.R.S.
- IV. "Note on the Trajectories of Rifled Projectiles with various Shapes of Head." By A. MALLOCK, F.R.S.

March 26, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The Bakerian Lecture—"On the Thermal and Electrical Conductivities of Metals and Alloys at Low Temperatures"—was delivered by Professor C. H. LEES, F.R.S.

The following Papers were read :—

- I. "Comparison of the Board of Trade Ampere-Standard Balance with the Ayrton-Jones Current-Weigher ; with an Appendix on the Electromotive Forces of Standard Cells." By T. MATHER, F.R.S., and F. E. SMITH.
 - II. "Note on the Ascent of Meteorological Balloons and the Temperature of the Upper Air." By A. MALLOCK, F.R.S.
-



April 2, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "Complete Survey of the Cell Lamination of the Cerebral Cortex of the Lemur." By Dr. F. W. MOTT, F.R.S., and Miss A. M. KELLEY.
- II. "The Alcoholic Ferment of Yeast-juice. Part III.—The Function of Phosphates in the Fermentation of Glucose by Yeast-juice." By A. HARDEN and W. J. YOUNG. Communicated by Dr. C. J. MARTIN, F.R.S.
- III. "Studies on Enzyme Action. XI.—The Hydrolysis of Raffinose. XII.—Emulsin." By Professor H. E. ARMSTRONG, F.R.S., and others.

The Society adjourned over the Easter Recess to Thursday, April 30.

April 30, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "On Scandium." By Sir WILLIAM CROOKES, F.R.S.
- II. "Note on the Representation of the Earth's Surface by means of Spherical Harmonics of the First Three Degrees." By Professor A. E. H. LOVE, F.R.S.
- III. "On the Hysteresis Loss and other Properties of Iron Alloys under very Small Magnetic Forces." By Professor E. WILSON, V. H. WINSON, and G. F. O'DELL. Communicated by Sir WILLIAM H. PREECE, K.C.B., F.R.S.
- IV. "The Relation between the Crystalline Form and the Chemical Constitution of the Picryl Derivatives." By G. JERUSALEM and Professor W. J. POPE, F.R.S.

- V. "The Condensation of certain Organic Vapours." By T. H. LABY.
Communicated by Professor J. J. THOMSON, F.R.S.
- VI. "A Photographic Determination of the Elements of the Orbits
of Jupiter's Satellites." By B. COOKSON. Communicated by
H. F. NEWALL, F.R.S.

May 7, 1908.

Annual Meeting for the Election of Fellows.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

The Statutes relating to the Election of Fellows having been read, Mr. Edward Saunders and the Hon. Robert John Strutt were, with the consent of the Society, nominated Scrutators, to assist the Secretaries in the examination of the balloting lists.

The votes of the Fellows present were collected, and the following Candidates were declared duly elected into the Society :—

| | |
|-------------------------|----------------------------------|
| Barlow, William. | Hamilton, David James. |
| Berkeley, Earl of. | Major, Charles Immanuel Forsyth. |
| Clerk, Dugald. | Nevill, Edmund Neville. |
| Dendy, Arthur. | Rivers, William Halse Rivers. |
| Dixon, Henry Horatio. | Russell, Hon. Bertrand Arthur W. |
| Gardiner, John Stanley. | Stapf, Otto. |
| Gowland, William. | Thorpe, Jocelyn Field. |
| Grace, John Hilton. | |

Thanks were given to the Scrutators.

May 7, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "Helium and Radio-activity in Rare and Common Minerals."
By Hon. R. J. STRUTT, F.R.S.
- II. "The Action of Resin and allied Bodies on a Photographic Plate
in the Dark." By Dr. W. J. RUSSELL, F.R.S.

- III. "Seleno-Aluminium Bridges." By Professor G. M. MINCHIN, F.R.S.
- IV. "A Tantulum Wave-detector, and its Application in Wireless Telegraphy and Telephony." By L. H. WALTER. Communicated by Professor J. A. EWING, C.B., F.R.S.
- V. "Percentage of the Inactive Gases in the Atmosphere: a Correction to Previous Calculations." By Sir WILLIAM RAMSAY, F.R.S.
- VI. "On the Use of Iridium Crucibles in Chemical Operations." By Sir WILLIAM CROOKES, F.R.S.
-

May 14, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

Professor Magnus Gustaf Retzius, elected Foreign Member in 1907, was admitted into the Society.

Mr. William Barlow, the Earl of Berkeley, Mr. Dugald Clerk, Professor Arthur Dendy, Professor William Gowland, Dr. David James Hamilton, Dr. Otto Stapf, and Dr. Jocelyn Field Thorpe were admitted into the Society.

A List of the Presents received was laid on the table, and thanks ordered for them.

The Croonian Lecture—"On the Structure of the Central Nervous System of the Higher and Lower Animals"—was delivered by Professor M. Gustaf Retzius, For. Mem. R.S.

May 21, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

Professor Henry Horatio Dixon and the Hon. Bertrand Russell were admitted into the Society.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read:—

- I. "On Some Features in the Hereditary Transmission of the Albino Character and the Black Piebald Coat in Rats." (Paper II.) By G. P. MUDGE. Communicated by Dr. A. D. WALLER, F.R.S.

- II. "A Further Note on the Nutrition of the Early Embryo, with special reference to the Chick." By E. EMRYS-ROBERTS. Communicated by Professor C. S. SHERRINGTON, F.R.S.
 - III. "The Antagonistic Action of Calcium upon the Inhibitory Effect of Magnesium." By S. J. MELTZER and J. AUER. Communicated by Professor E. H. STARLING, F.R.S.
-

May 28, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

Dr. C. I. Forsyth Major was admitted into the Society.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "On the Theory of Capillarity." By Professor E. T. WHITTAKER, F.R.S.
 - II. "Effect of a Cross Wind on Rifled Projectiles." By A. MALLOCK, F.R.S.
 - III. "Transparent Silver and other Metallic Films." By Professor T. TURNER. Communicated by Professor J. H. POYNTING, F.R.S.
-

June 4, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

Mr. John Stanley Gardiner and Mr. John Hilton Grace were admitted into the Society.

M. Henri Becquerel, Professor Friedrich Robert Helmert, Professor S. Kitasato, and Dr. Samuel Weir Mitchell were elected Foreign Members of the Society.

The following Papers were read :—

- I. "On the Aberration of Sloped Lenses, and on their Adaptation to Telescopes of Unequal Magnifying Power in Perpendicular Directions." By the LORD RAYLEIGH, O.M., Pres.R.S.
- II. "The Optical Constants of Gypsum at Different Temperatures, and the Mitscherlich Experiment." By Dr. A. E. H. TUTTON, F.R.S.
- III. "On the Viscosity of Ice." By R. M. DEELEY. Communicated by Dr. H. WOODWARD, F.R.S.
- IV. "The Effect of Temperature on the Neutralisation-volume Change for Different Salts at Different Concentrations." By Miss IDA FREUND. Communicated by F. H. NEVILLE, F.R.S.
- V. "Note on a New Sounding Machine for Use on Lakes and Rivers without a Boat." By Professor E. J. GARWOOD. Communicated by Professor T. G. BONNEY, F.R.S.
- VI. "The Electrical Qualities of Porcelain, with Special Reference to Dielectric Losses." By H. F. HAWORTH. Communicated by Professor W. E. AYRTON, F.R.S.
- VII. "On the Decay of the Radium Emanation when Dissolved in Water." By R. B. MOORE. Communicated by Sir WILLIAM RAMSAY, K.C.B., F.R.S.

The Society adjourned over the Whitsun Recess to Thursday, June 18.

June 18, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

Professor Grafton Elliot Smith (elected 1907) was admitted into the Society.

The following Papers were read :—

- I. "An Electrical Method of Counting the Number of α Particles from Radio-active Substances." By Professor E. RUTHERFORD, F.R.S., and Dr. HANS GEIGER.
 - II. "The Charge and Nature of the α Particle." By Professor E. RUTHERFORD, F.R.S., and Dr. HANS GEIGER.
 - III. "On the Scattering of the α Particles by Matter." By Dr. HANS GEIGER. Communicated by Professor RUTHERFORD, F.R.S.
 - IV. "Studies of the Processes operative in Solutions. Part VI.—Hydration, Hydration and Hydrolysis as Determinants of the Properties of Aqueous Solutions. VII.—The Relative Efficiencies of Acids as deduced from their Conductivities and Hydrolytic Activities. VIII.—The Influence of Salts on Hydrolysis, and the Determination of Hydration Values. IX.—The Determination of Optical Rotatory Power in Solutions. X.—The Changes effected by the Reciprocal Interference of Cane-sugar and other Substances (Salts and Non-electrolytes)." By Professor H. E. ARMSTRONG, F.R.S., and others.
 - V. "The Electrolytic Properties of Dilute Solutions of Sulphuric Acid." By W. C. D. WHETHAM, F.R.S., and H. H. PAINE.
 - VI. "The Giant Nerve Cells and Fibres of *Halla parthenopeia*." By Dr. J. H. ASHWORTH. Communicated by Professor J. C. EWART, F.R.S.
 - VII. "On Methods for the Continuous (Photographic) and Quasi-continuous Registration of the Diurnal Curve of the Temperature of the Animal Body." By Professor A. GAMGEE, F.R.S.
-

June 25, 1908.

LORD RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "Have Trypanosomes an Ultra-microscopical Stage in their Life-History ?" By Colonel D. BRUCE, C.B., F.R.S., and Captain H. R. BATEMAN.
- II. "A Search for Possible New Members of the Inactive Series of Gases." (Introductory Note to the Papers by Mr. H. E. WATSON and Professor R. B. MOORE.) By Sir WILLIAM RAMSAY, K.C.B., F.R.S.
- III. "The Spectrum of the Lighter Constituents of the Atmosphere." By H. E. WATSON. Communicated by Sir WILLIAM RAMSAY, K.C.B., F.R.S.
- IV. "An Investigation of the Heavier Constituents of the Atmosphere." By Professor R. B. MOORE. Communicated by Sir WILLIAM RAMSAY, K.C.B., F.R.S.
- V. "On the Atomic Weight of Chlorine." By Dr. E. C. EDGAR. Communicated by Professor H. B. DIXON, F.R.S.
- VI. "Note on the Vapour Pressure and Osmotic Pressure of a Volatile Solute." By Professor H. L. CALLENDAR, F.R.S.
- VII. "Eutectics Research No. 1: Alloys of Lead and Tin." By W. ROSENHAIN and P. A. TUCKER. Communicated by Dr. R. T. GLAZEBROOK, F.R.S.
- VIII. "The Emission and Transmission of Röntgen Rays." By G. W. C. KAYE. Communicated by Professor J. J. THOMSON, F.R.S.
- IX. "Further Note on a Luminous Glow generated by Electrostatic Induction in an Exhausted Vessel made of Silica." By Rev. F. J. JERVIS-SMITH, F.R.S.
- X. "The Action of Chlorine upon Urea whereby a Dichloro Urea is produced." By Dr. F. D. CHATTAWAY, F.R.S.
- XI. "On the Reflection of Waves from a Stratum of Gradually Varying Properties, with Application to Sound." By Dr. J. W. NICHOLSON. Communicated by Professor J. LARMOR, Sec.R.S.

- XII. "Preliminary Account of the Habits and Structure of the Anaspidiida, with Remarks on some other Fresh-water Crustacea from Tasmania." By GEOFFREY W. SMITH. Communicated by Professor E. B. POULTON, F.R.S.
- XIII. "The Ω -functions—a Class of Normal Functions." By E. CUNNINGHAM. Communicated by Professor K. PEARSON, F.R.S.
- XIV. "Diphtheria Antitoxin." By D. J. MELLANBY. Communicated by Professor J. N. LANGLEY, F.R.S.
- XV. "The Boiling-point of Sulphur on the Constant-pressure Air-thermometer." By N. EUMORFOPOULOS. Communicated by Professor CALLENDAR, F.R.S.
- XVI. "Note on the Boiling-point of Sulphur." By Professor H. L. CALLENDAR, F.R.S.
- XVII. "A Study of the Variations in the Secretion of Hydrochloric Acid in the Gastric Contents of Mice and Rats as compared with the Human Subject in Cancer." By Dr. S. M. COPEMAN, F.R.S., and Dr. H. W. HAKE.
- XVIII. "The Spectrum of Scandium and its Relation to Solar Spectra." By Professor A. FOWLER. Communicated by Sir W. CROOKES, F.R.S.
- XIX. "Note on the Instability of Tubes subjected to End Pressure, and on the Folds in a Flexible Material." By A. MALLOCK, F.R.S.

The Society adjourned over the Long Vacation to Thursday, November 5.

PROCEEDINGS OF THE ROYAL SOCIETY.

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MATHEMATICAL AND PHYSICAL SCIENCES.

CONTENTS.

| | Page |
|--|------|
| On the Measurement of the Atmospheric Electric Potential Gradient and the Earth-air Current. By C. T. R. WILSON, F.R.S. | 537 |
| On the Hysteresis Loss and other Properties of Iron Alloys under very Small Magnetic Forces. By Professor ERNEST WILSON, V. H. WINSON, and G. F. O'DELL | 548 |
| Note on the Representation of the Earth's Surface by Means of Spherical Harmonics of the First Three Degrees. By A. E. H. LOVE, F.R.S. | 553 |
| The Relation between the Crystalline Form and the Chemical Constitution of the Picryl Derivatives. By GEORGE JERUSALEM and WILLIAM JACKSON POPE, F.R.S., Professor of Chemistry, Municipal School of Technology, Victoria University of Manchester | 557 |
| A Photographic Determination of the Elements of the Orbits of Jupiter's Satellites. By BRYAN COOKSON, M.A., Mackinnon Student, July, 1904—July, 1906 | 567 |
| Helium and Radio-activity in Rare and Common Minerals. By the Hon. R. J. STRUTT, F.R.S. | 572 |
| Effect of a Cross Wind on Rifled Projectiles. By A. MALLOCK, F.R.S. | 595 |
| On the Decay of the Radium Emanation when dissolved in Water. By RICHARD B. MOORE, B.Sc. | 597 |
| Percentage of the Inactive Gases in the Atmosphere: a Correction to Previous Calculations. By Sir WILLIAM RAMSAY, F.R.S. | 599 |
| Index | lxv |
| Title, Contents, etc. | |

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June 20, 1908.

NOTICE TO AUTHORS AND COMMUNICATORS.

The Council has had under consideration the rapid increase of the Society's expenditure on publications. In view of the necessity for economy, authors of papers are urgently requested to see that their communications are put in as concise a form as possible. Delay in decisions regarding publication, as well as subsequent trouble to authors, is often caused by diffuseness or prolixity. MSS. must be type-written or at least written in a legible hand, and properly prepared as copy for press. Type-written transcript should in all cases be carefully revised by the author before being presented. It is desirable that authors should retain copies of their MSS. for reference.

Authors are further requested to send in all drawings, diagrams or other illustrations in a state suitable for direct photographic reproduction. They should be drawn on a large scale in Indian ink on a smooth white surface, with lettering adapted to a reduction in scale. Great care should be exercised in selecting only those that are essential. Where the illustrations are numerous, much time would be saved if the authors would indicate in advance those which, if a reduction of their number is found to be required, might be omitted with least inconvenience.

"It shall be the duty of each Fellow or Foreign Member to satisfy himself that any letter, report or other paper which he may communicate, is suitable to be read before the Society,"—Statute VI, Cap. xii.

NOTICES TO FELLOWS OF THE ROYAL SOCIETY.

The Council have directed that the Minutes of the Meetings of the Society shall be sent out as an inset in the 'Proceedings,' separately paged, and shall afterwards be republished in the 'Year-Book.'

The 'Proceedings,' both the Physical and the Biological Series, are sent in the ordinary course by post to every Fellow of the Society who resides within the limits of the Postal Union. On application to Messrs. Harrison and Sons, 45, St. Martin's Lane, these will be bound in volumes, in cloth, for 2s. 6d., or the cases for binding may be purchased, price 1s. 6d.

The 'Philosophical Transactions' are delivered, in volumes, in cloth covers, only to those Fellows who call for them, or who send a written application to the Assistant Secretary. Such an application may, if so desired, be filed as a standing order.

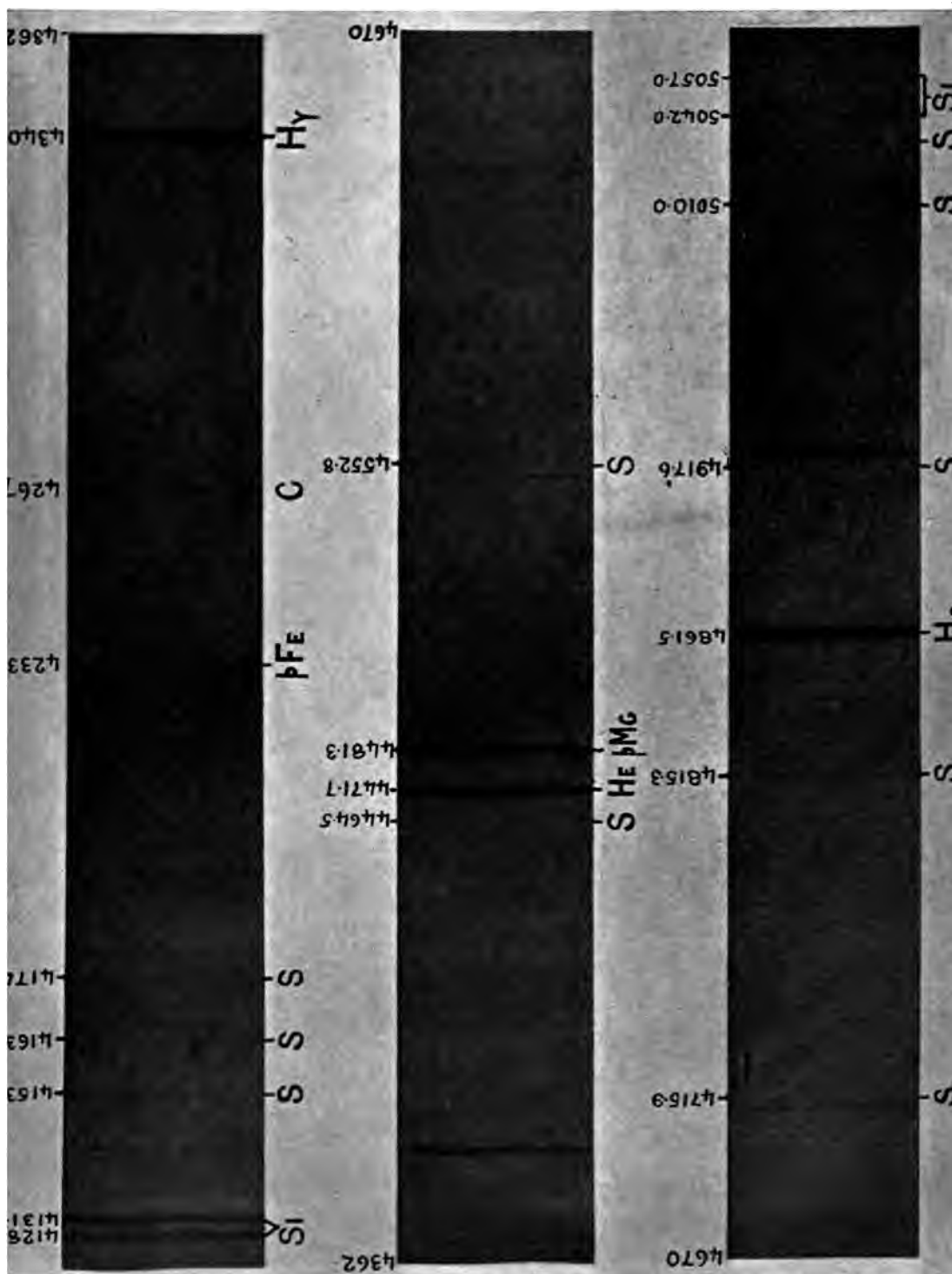
The 'Philosophical Transactions' are also delivered in the form of separate Papers, post free, immediately on publication, to those Fellows who desire to have them in that form. And, on application to Messrs. Harrison and Sons, 45, St. Martin's Lane, these will be bound in a cloth case for 2s. 6d., or the cloth cases for binding may be purchased, price 1s. 6d.

SUBSCRIPTION TO THE PUBLICATIONS OF THE ROYAL SOCIETY.

Series A of the 'Proceedings' may be subscribed for in advance, by the public, at the reduced uniform price of 15s. per volume of about 600 pages.

Series B of the 'Proceedings' may be subscribed for at the reduced uniform price of 20s. per volume.

Each Series of the 'Proceedings' may be obtained, for this subscription, either in separate numbers, immediately on publication, or in volumes, bound in blue cloth if desired. About two volumes of each Series appear per annum. Cases for binding can be purchased as above.





In general, it is clear that

$$\begin{aligned} & \frac{p!}{\pi!} (\phi\xi)^\pi \phi_x^{p-\pi} \cdot \psi_x^q \\ &= (-)^\pi \frac{q!}{\pi!} (\psi\xi)^\pi \psi_x^{q-\pi} \cdot \phi_x^p, \\ &= \frac{p!}{\pi!} \frac{q!}{\pi!} (\phi\psi)^\pi \phi_x^{p-\pi} \psi_x^{q-\pi}; \end{aligned}$$

or, as it may be otherwise written,

$$\begin{aligned} & \frac{\pi!}{q!} (\phi\xi)^\pi \phi_x^{p-\pi} \cdot \psi_x^q, \\ &= (-)^\pi \frac{\pi!}{p!} (\psi\xi)^\pi \psi_x^{q-\pi} \cdot \phi_x^p, \\ &= (\phi\psi)^\pi \phi_x^{p-\pi} \psi_x^{q-\pi}; \end{aligned}$$

showing that the π th transvectant of two forms is obtainable by a pure operation upon either of the forms.

So far as the writer is aware, such a transvection has not hitherto been exhibited as the result of a pure operation. The importance of the operational invariant

$$(a\xi)^\pi a_x^{n-\pi}$$

is thus evident.



0.00645 and 0.0121 respectively, which compare well with the values given in Table II. The same apparatus gave the following results for mercury at high temperatures :—

Table III.—Mercury at High Temperatures.

| Temperature. | Logarithmic decrement. | Logarithmic decrement minus the value for air and corrected for expansion. | Density. | Absolute viscosity according to Koch.* | Absolute viscosity calculated from logarithmic decrement. |
|--------------|------------------------|--|----------|--|---|
| ° C. | | | | | |
| 65 | 0.1632 | 0.1526 | 13.48 | 0.0136 | 0.0138 |
| 95 | 0.1538 | 0.1431 | 13.39 | 0.0125 | 0.0124 |
| 133 | 0.1481 | 0.1373 | 13.27 | 0.0114 | 0.0116 |
| 216 | 0.1413 | 0.1302 | 13.08 | 0.0100 | 0.0106 |

* 'Ann. der Physik,' 1881, vol. 14, pp. 1—12.

An example of a determination of viscosity at a somewhat higher temperature is given in Table IV. The values of the density and viscosity for sodium nitrate have already been determined by the capillary method.* These values are given in the table along with the values of viscosity calculated from the logarithmic decrements using the same density values. The disc used was one of fireclay, 27 mm. in diameter. The constants C_1 , C_2 , and C_3 , as determined by oscillations in water, mercury, and chloroform, were

$$C_1 = 0.4595, \quad C_2 = 1.238, \quad C_3 = -0.2052.$$

Table IV.—Sodium Nitrate (Melting Point 309° C.).

| Temperature. | Logarithmic decrement. | The same minus value for air. | The same corrected for expansion. | Density (Goodwin and Mailey). | Viscosity (Goodwin and Mailey). | Viscosity (from logarithmic decrement). |
|--------------|------------------------|-------------------------------|-----------------------------------|-------------------------------|---------------------------------|---|
| ° C. | | | | | | |
| 320 | 0.1440 | 0.1335 | 0.1337 | 1.91 | 0.0282 | 0.0291 |
| 358 | 0.1255 | 0.1150 | 0.1146 | 1.89 | 0.0227 | 0.0228 |
| 390 | 0.1180 | 0.1075 | 0.1071 | 1.86 | 0.0191 | 0.0205 |
| 435 | 0.1053 | 0.0948 | 0.0944 | 1.83 | 0.0160 | 0.0165 |
| 450 | 0.1022 | 0.0917 | 0.0914 | 1.82 | 0.0152 | 0.0156 |

The numbers in the last two columns agree within the experimental error. These results show the availability of this method for the determination

* Goodwin and Mailey, *loc. cit.*

298 *On the Determination of Viscosity at High Temperatures.*

of viscosity up to the highest temperature at which a platinum capillary has been used. As the fireclay or graphite disc remains uncorroded at temperatures of 1000° C. and over, the method is quite well suited for high temperature work. I am now engaged on viscosity measurements with a number of salts and metals, and hope before long to report on these.

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